Theoretical Studies on the Spin and Electron Correlations in Doublet Radicals and Various Excited States(Dissertation_全文)

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PREFACE

The quantitative prediction of various chemical phenomena is one of the main purposes of theoretical chemistry based on the quantum theory. In the history of the theoretical chemistry, molecular orbital (MO) theory has played an important role because of its physical simplicity and visuality. Most aspects of atomic and molecular theories are understood in terms of orbitals, i. e. independent motion of electrons in the average fields. As is well known now, for quantitative theory this is not sufficient and the electron correlation should be introduced to wavefunctions. Among the many correlation theories, Sinanoglu's many electron theory (MET) in 1962 is one of the most important studies and has influenced many theoretical studies thereafter. Recently, symmetry-adapted-cluster (SAC) expansion theory has been developed by Nakatsuji and Hirao. The SAC theory is the generalization of the cluster expansion theory to the spin and electron correlations in open-shell and various excited states and considers the self-consistency effect of the symmetry-adapted linked operators correctly. SAC-CI theory has also been developed by Nakatsuji in 1978. The wavefunction of the SAC-CI theory is constructed from the excited functions, which are orthogonal and hamiltonian-orthogonal to the SAC wavefunction of the ground state, and satisfies the necessary conditions of wavefunctions for excited states. The SAC-CI theory thus gives more rapidly convergent wavefunction of the excited state than the ordinary CI method.

Another important factor in the history of the theoretical

chemistry is a remarkable development of electronic computers. In the first half of 1970's, Hartree Fock (HF) theory has been applied, based on ab initio calculations, to many systems of chemical interests and not only its effectiveness but also its theoretical limitations have been recognized clearly. From the second half of 1970's, ab initio calculations of the electronic wavefunction beyond the HF theory have been carried out extensively. It gave one of the most powerful methods to predict various chemical phenomena quantitatively.

In the present thesis, the author studies the spin and electron correlations in open-shell systems and various excited states by the SAC and SAC-CI theories. All of the calculations were carried out by the ab initio method. The text has been divided into four parts.

The first part presents the studies on the spin correlations considered by pseudo-orbital (PO) theory which includes only one-electron excitations within the SAC expansion theory. Spin densities of organic and inorganic radicals have been investigated. Spin correlation effects of the conventional open-shell orbital theories, first-order-perturbation theory, and singly excited (SE) CI theory were discussed in comparison with that of the PO theory. Calculated spin densities by the PO theory were in fair agreement with experiments and were much better than the results of the conventional orbital theories. This shows that the PO theory takes into account the spin correlation correctly within the orbital theoretic framework.

In part II, not only the spin correlation effect but also the electron correlation effect are studied by the SAC and

SAC-CI theories. The purpose of this part is to study the spin and electron correlations at the same time and investigate the coupling effect of these two correlations. Calculation was performed for BeH, NH_2, CH_3, CH_2CH, CH_3CH_2, HCO, and NO_2 radicals. The calculated excitation energies, ionization potentials, and spin densities agreed well with experiments. Important spin distributions were improved in comparison with the results of the PO theory, showing that the coupling effects of spin and electron correlations are important.

Part III presents the studies on the electron correlations in the various excited states. Singlet and triplet excited states, Rydberg excited states, ionized states, and electron attached states of formaldehyde have been studied by the SAC and SAC-CI theories. Rydberg excited states and ionized states of NH_2 and CH_3 radicals have also been studied. The results compared well with experiments and it was ascertained through the quantitative calculation that the SAC and SAC-CI theories describe the electron correlation effect adequetly in the various kinds of excited states.

In part IV, the PO theory has been applied to the studies of the geometries and hyperfine splitting (hfs) constants of doublet radicals of chemical interests. The spin correlation in radicals which have a heavy element has been studied in CH_3, SiH_3, and GeH_3 radicals. In CH_3 and SiH_3 radicals the spin polarization of inner-shells is not always small and varied largely as the molecular geometries changed. On the other hand, for GeH_3, the spin polarization in the valence-shell plays a dominant role and the polarization in the inner-shells is

negligible. Vibrational effects on the hfs constants were found to be large especially for the central elements of these radicals. Jahn-Teller effects on the molecular structure and hfs constants of the cation radicals of cyclopropane, cyclobutane, and cyclopentane have also been studied. These are σ radicals and large spin densities were calculated by the PO theory reflecting the large Jahn-Teller distortions in the molecular geometries.

General conclusions of these investigations are given at the end of this thesis.

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THEORETICAL STUDIES ON THE SPIN AND ELECTRON CORRELATIONS

IN

DOUBLET RADICALS AND VARIOUS EXCITED STATES

CONTENTS

LIST OF PUBLICATIONS

PART I.

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PART I

SPIN CORRELATIONS OF DOUBLET RADICALS

CHAPTER 1

INTRODUCTION

Spin correlation problem in open-shell systems has been one of the most interesting objects in quantum chemistry. The conventional open-shell orbital theories such as the unrestricted HF (UHF) theory[1] or the spin-extended (SE) HF[2] theory have theoretical defects analized previously[3]. The UHF wavefunction does not satisfy spin symmetry and it usually gives spin densities larger than the experimental values. In the SEHF theory, the spin correlation effect and the electron correlation effect interfere with each other through the variational process, so that only poor results are obtained for both spin densities and correlation energies[4b]. In Part I, we study the spin correlation problem by the pseudo-orbital (PO) theory[4a,b]. It considers only one-electron excitation operators within the symmetry-adapted-cluster (SAC)[4b] expansion theory and belongs to one of the orbital theoretic approaches based on the Thouless' theorem. In chapter 2, the spin correlations of various σ and π radicals are studied by the calculation of hyperfine splitting constants of ESR. The PO theory used here containes the spin-polarized excitation operators and their unlinked terms up to second order. In Chapter 3, the higher order effect of the spin-polarized excitation operators are investigated by solving the linearized variational equation iteratively with the use of natural orbitals. Operators which contribute to the spin-delocalization directly have also included with their

higher order terms though they do not contribute in first order since they satisfy the Brillouin theorem for HF wavefunction.

References

1. J.A.Pople and R.K.Nesbet, J.Chem.Phys. 22, 571 (1954).

2. P.-O.Lowdin, Phys.Rev. 97, 1490, 1509 (1955); R.Pauncz, Alternant Molecular Orbital Method (Saunders, Philadelphia); K.M.Sando and J.E.Harriman, J.Chem.Phys. 47, 180 (1967); U.Kaldor, J.Chem.Phys. 48, 835 (1968).

3. (a) H.Nakatsuji, H.Kato, and T.Yonezawa, J.Chem.Phys. 51, 3175 (1969). (b) H.Nakatsuji, J.Chem.Phys. 59, 2586 (1973).

4. (a) H.Nakatsuji and K.Hirao, Chem.Phys.Lett. 47, 569 (1977). (b) H.Nakatsuji and K.Hirao J.Chem.Phys. 68, 2053, 4279 (1978).

PART I, Chapter 2

Spin Densities of Organic and Inorganic Radicals Studied by the Pseudo-Orbital Theory

I. INTRODUCTION

The isotropic hyperfine splitting (hfs) constants of free radicals have been the subject of a number of *ab initio* studies.[1-7] The calculations have been carried out with the conventional open-shell orbital theories, the first-order perturbation theory, and the single excitation (SE) CI theory. The conventional open-shell orbital theories such as the unrestricted HF (UHF) theory[8] or the spin-extended (SE) HF theory[9] have theoretical defects as analyzed previously.[10,11] The UHF wave function does not represent a pure spin symmetry. It usually gives spin densities larger than the experimental values. In the SEHF theory, the spin-correlation effect and the electron-correlation effect interfere with each other through the variational process, so that only poor results are obtained for both spin densities and correlation energies.[1,12,13] On the other hand, the spin-polarization single excitation (SE) CI theory does not include the self-consistency of the spin-polarization effect. The first-order perturbation theory is dependent on the unitary transformations among orbitals (e.g., canonical orbitals and localized orbitals). Such dependence can be eliminated if the single excitation CI matrix is diagonalized completely.[14]

In the previous works,[15,16] we have proposed a new open-shell orbital theory based on the symmetry-adapted-cluster (SAC) expansion of an exact wave function. This theory has been called pseudo-orbital (PO) theory. It does not share the theoretical defects with the conventional open-shell orbital theories. For the first-row atoms, the pseudo-orbital (PO) theory has given spin densities which are fairly better than those of the UHF, SEHF, and SECI theories.[16]

In this work, we extend the calculation to a variety of σ and π radicals of organic and inorganic molecules. For comparison, we have also calculated hfs constants by the UHF, projected UHF (PUHF), and SECI theories. In Sec. II, we outline the pseudo-orbital (PO) theory applied in this work. In Sec. III, we first discuss the selection of the Gaussian basis set which is suitable for the calculation of the hfs constants, and then compare the present results with those of previous *ab initio* studies. In Sec. IV, we give the results of the hfs constants of organic and inorganic σ and π radicals. The conclusions of the present study are given in Sec. V.

II. THEORETICAL BACKGROUND

A. Pseudo-orbital theory

The basis of the pseudo-orbital (PO) theory has been discussed in detail in Refs. 15 and 16. Thouless[17] has shown that, if only the one-particle excitation operator $\hat{T}_1$ is considered in the conventional cluster expansion, i.e.,

$$\Psi = N \exp(\hat{T}_1)\Phi_0 \quad , \tag{1}$$

it is equivalent to a transformation of a single determinant Φ_0 to another single determinant Ψ. Thus, when we apply the variational principle to the cluster expansion (1), the resultant Ψ should be equivalent to the HF wave function. In open-shell systems, the resultant HF wave function is the UHF wave function. The SAC expansion is an extension of the cluster expansion to open-shell systems.[15] It is different from the conventional cluster expansions. The symmetry adaptation is essential because of the nonlinear character of the expansion. The PO theory has been derived, analogously based on Eq. (1), by considering only the single excitation operators in the SAC expansion formalism (see Fig. 1),

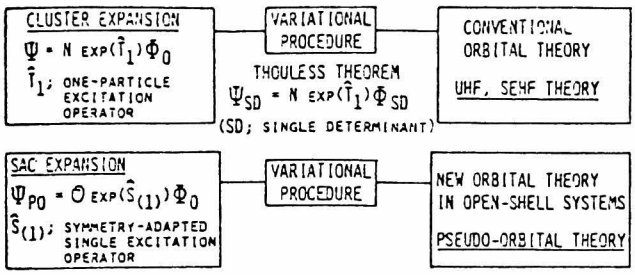


FIG. 1. The concept of the pseudo-orbital theory.

namely,

$$\Phi_{PO} = \mathcal{O} \exp(\hat{S}_{(1)})\Phi_0 \quad . \tag{2}$$

The operator $\hat{S}_{(1)}$ is expanded by the symmetry-adapted single excitation operator $S^{\dagger}_{\sigma_1,i}$ as

$$\hat{S}_{(1)} = \sum_{\sigma_1}^{f_1} \sum_{i} C_{\sigma_1,i} S^{\dagger}_{\sigma_1,i} \quad , \tag{3}$$

where σ_1 denotes an element of the f_1 independent (degenerate) symmetry functions of the single excitations i. In the present calculations, we have adopted only the spin-polarization excitation operator $S^{\dagger}_{P,tk}$ for the $S^{\dagger}_{\sigma_1,i}$, namely ,

$$\begin{aligned} \Psi_{PO3} &= \mathcal{O} \exp\left(\sum_{i} \sum_{k} C_{P,tk} S^{\dagger}_{P,tk} \right) \Phi_0 \\ &= \mathcal{O} \exp\left(\sum_{I} C_I S^{\dagger}_I \right) \Phi_0 \quad , \end{aligned} \tag{4}$$

$$\begin{aligned} S^{\dagger}_{P,tk} = (s+2)^{-1/2} \Big[& (s/2)^{1/2} (a^{\dagger}_{t\alpha} a_{k\alpha} - a^{\dagger}_{t\beta} a_{k\beta}) \\ & + (2/s)^{1/2} a^{\dagger}_{t\alpha} a_{k\beta} \sum_{m=q+1}^{p} a^{\dagger}_{m\beta} a_{m\alpha} \Big] \quad , \end{aligned} \tag{5}$$

where the excitation operator $S^{\dagger}_{P,tk}$ generates the spin-adapted spin-polarization excitation from doubly occupied orbital k to vacant orbital t. s denotes the number of unpaired electrons in the system (i.e., $s=1$ for doublet and $s=2$ for triplet). The other types of single excitations were neglected since they satisfy the Brillouin theorem for the restricted HF wave function[16,13] chosen here for the reference wavefunction Φ_0:

$$\Phi_0 = |0\rangle = \| \phi_1\alpha\phi_1\beta \cdots \phi_k\alpha\phi_k\beta \cdots \phi_q\alpha\phi_q\beta\phi_{q+1}\alpha \cdots \phi_p\alpha \| . \tag{6}$$

When the system has degenerate spatial symmetry, a linear combination of the $S^{\dagger}_{p,tk}$ given by Eq. (5) is necessary for the symmetry adaptation. For example, the methyl radical has D_{3h} symmetry and the symmetry-adapted (a_1') excitation operator from the degenerate doubly occupied MO pair (k_x, k_y) to the degenerate vacant MO pair (t_x, t_y) is written as

$$S^{\dagger}_{P,(t_x,t_y)(k_x,k_y)} = 2^{-1/2} (S^{\dagger}_{P,t_xk_x} + S^{\dagger}_{P,t_yk_y}) \quad . \tag{7}$$

However, when we adopt a linear approximation in the variational equation [see Eq. (10)], the space symmetry is automatically satisfied and Eq. (7) is not necessarily required. In the variational equation which considers more than second order in the coefficients, the symmetry adaptation as Eq. (7) is inevitably necessary.

We apply the variational principle to solve the PO wave function Ψ_{PO3} and obtain[15]

$$\langle \Psi_{PO3} | (H - E) S^{\dagger}_I | \Psi'_{PO3} \rangle = 0 \quad , \tag{8}$$

for all I included in Eq. (4). Here Ψ'_{PO3} is given by

$$\Psi'_{PO3} = \exp\left(\sum_{I} C_I S^{\dagger}_I \right) \Phi_0 \quad , \tag{9}$$

which does not have the projection operator $\mathcal{O}$ in front of the unlinked terms. When the reference wave function Φ_0 is already a reasonably good wave function, the coefficient C_I would be small so that we may neglect the second- and higher-order terms in Eq. (8). Thus, retaining terms up to first order in the coefficients, we obtain from Eq. (8) the linear equation

$$\begin{aligned} \langle 0 | H S^{\dagger}_I | 0 \rangle + \sum_{J} C_J (& \langle 0 | S_J H S^{\dagger}_I | 0 \rangle \\ & + \langle 0 | H S^{\dagger}_I S^{\dagger}_J | 0 \rangle - E\delta_{IJ}) = 0 \quad , \end{aligned} \tag{10}$$

for all I included in Eq. (4). Further, we define the H matrix and the normalized eigenvector D as

$$\begin{aligned} & H_{0I} = \langle 0 | H S^{\dagger}_I | 0 \rangle \quad , \\ & H_{IJ} = \langle 0 | S_J H S^{\dagger}_I | 0 \rangle + \langle 0 | H S^{\dagger}_I S^{\dagger}_J | 0 \rangle \quad , \\ & D = d_0 (1, C_1, C_2, \cdots, C_N) \quad . \end{aligned} \tag{11}$$

Then, Eq. (10) is reduced to the secular equation

$$(H - E) D = 0 \quad . \tag{12}$$

A diagonalization of Eq. (12) leads to the energy E and the coefficients $C_{P,tk}$. This solution is simpler than the previous one in a sum-over-state form.[15]

On the other hand, the SECI wave function does not include the self-consistency effect of the symmetry-adapted excitation operator $S^{\dagger}_I$. As analyzed previously,[16] it usually gives spin densities smaller than those of the PO theory. The secular equation for the SECI theory is

$$\langle 0 | H S^{\dagger}_I | 0 \rangle + \sum_{J} C_J (\langle 0 | S_J H S^{\dagger}_I | 0 \rangle - E\delta_{IJ}) = 0 \quad . \tag{13}$$

Thus, by dropping off the first-order self-consistency term, i.e., $\langle 0 | H S^{\dagger}_I S^{\dagger}_J | 0 \rangle$, from Eq. (10), we obtain the results for the SECI theory.

In order that the calculated results are independent of the unitary transformations among orbitals, the secular equation (12) should be diagonalized completely without neglecting the off-diagonal terms.[14] The present results are thus independent of such transformations. The first-order perturbation theory used by Ellinger *et al.*[6] are dependent on the unitary transformations among orbitals (e.g., canonical and quasilocalized representations). The dependence is very large. Such dependence is not preferable and should be deleted.

B. Spin density

We have calculated spin densities correct to second order in the coefficients. From Eq. (4), we obtain the spin density as

$$\begin{aligned} & \rho(r) = \rho_{3D}(r) + \rho_{3P}(r) \quad , \\ & \rho_{3D}(r) = d_0^2 \langle 0 | \hat{\rho}(r) | 0 \rangle = (d_0^2/s) \sum_{m} \phi^2_m(r) \quad , \end{aligned}$$

$$\rho_{SP}(r) = d_0^2\left[2\sum_I C_I\langle 0|S_I\hat{\rho}(r)|0\rangle + \sum_I\sum_J C_I C_J\langle 0|S_I\hat{\rho}(r)S_J^*|0\rangle\right] = (d_0^2/s)\Big(2(2s/(s+2))^{1/2}\sum_I C_I\phi_k(r)\phi_t(r)$$
$$+\sum_I\sum_J C_I C_J\Big\{\delta_{tu}\delta_{kl}[(s^2+2s-4)/(s^2+2s)]\sum_m\phi_m^2(r) + [2/(s+2)][\delta_{tu}\phi_l(r)\phi_k(r) + \delta_{kl}\phi_t(r)\phi_u(r)]\Big\}\Big) \quad , \tag{14}$$

where $I=(P, tk)$, $J=(P, ul)$, and $\hat{\rho}$ denotes the normalized spin density operator

$$\hat{\rho}(r) = (2/s)\sum_\nu S_z(\nu)\delta(r - r_\nu). \tag{15}$$

The subscripts SD and SP mean the spin-delocalization and the spin-polarization contributions, respectively.[10,19] The spin-delocalization term ρ_{SD} arises from the delocalization of the unpaired-spin orbitals over the molecules and is always positive or zero. The spin-polarization term ρ_{SP} arises from the spin-correlation correction to the restricted HF (RHF) wave function. It is either positive or negative. In the case of π radicals, the ρ_{SD} contribution is zero (for the nuclei on the plane), and the spin density is determined only by the spin-polarization term ρ_{SP}.

The hfs constants and the spin densities are connected by the following equation:

$$a^N = (8\pi/3)(g_e/g_0)g_N\beta_N\rho(r_N) \quad , \tag{16}$$

where (g_e/g_0) is the ratio of the g values of the free electron and the radical under consideration and will be taken as unity hereafter; g_N and β_N are the nuclear magnetogyric ratio and nuclear magneton, respectively. Specifically, $a^H = 1592.2\rho(H)$, $a^C = 400.4\,\rho(^{13}C)$, $a^N = 115.0\,\rho(^{14}N)$, $a^O = -215.9\,\rho(^{17}O)$, and $a^F = 1497.9\,\rho(^{19}F)$, where a is in G and ρ in a.u.

III. CALCULATIONS AND RESULTS FOR CH_3 RADICAL

For the *ab initio* calculation of hfs constants of molecules, the selection of the basis set is as important as the selection of the good theory. This is seen in Table I which summarizes the previous *ab initio* calculations of the hfs constant of methyl radical together with the present one.

We have determined the basis set based on the calculation of the hfs constant of the methyl radical in its planar geometry.[20] The Gaussian basis set, consisting of Huzinaga's (9s5p/4s) set,[21] was contracted in several ways to [4s2p] on carbon and to [2s] on hydrogen. In Table II, the effects of contraction on the calculated hfs constants of the methyl radical are given. The best basis set for carbon is the [9s5p] uncontracted basis set [(D) in Table II]. The calculated hfs constant is 37.9 G. The best basis set for hydrogen is [4s] uncontracted basis set [(E) in Table II]. The calculated value is

TABLE I. *Ab initio* calculation of hfs constants (in G) of planar CH_3.

Reference	Basis set	Method	a(H)	a(C)
Chang, Davidson, and Vincow[4]	minimal STO (Slater rule)	SECI	−29.2	133.6
	minimal STO (optimized)	SECI	−38.9	132.3
	double ζ STO	SECI	−36.1	23.0
Konishi and Morokuma[5]	minimal STO+S	SECI	−29.6	62.3
	double ζ STO+2S	SECI	−27.6	35.6
Millie, Levy, and Berthier[5(a)]	[6s4p2d/3s1p] (CGTO)	FOP[a] canonical	−20.6	10.2
		quasilocalized	−13.0	−5.0
Ellinger, Rassat, Subra and Berthier[5(b)]	[4s2p/2s] (CGTO)	FOP canonical	−24.6	9.7
	$\zeta_H = 1.0$	quasilocalized	−31.0	31.0
This work	[4s2p/2s] $\zeta_H = 1.2$	pseudo-orbital	−26.5	39.4
		UHF	−40.6	71.3
		PUHF	−13.2	24.8
		SECI	−24.3	33.3
Fessenden[25(a)]		Exptl.	−23.0	38.3

[a]First-order perturbation.

TABLE II. Hyperfine splitting constant (in G) and energy (a.u.) calculated by the pseudo-orbital theory with various contraction of the primitive Gaussian set ($\zeta_H = 1.0$).

Contraction type	a(H)	a(C)	Energy
(A)	−25.7	38.4	−39.5211
(B)	−26.8	41.7	−39.5412
(C)	−31.5	36.4	−39.5500
(D)	−27.2	37.9	−39.5451
(E)	−25.7	36.7	−39.5538

(A) C, $(9s5p)-[5211/32]$; H, $(4s)-[22]$.

(B) C, $(9s5p)-[6111/41]$; H, $(4s)-[22]$.

(C) C, $(9s5p)-[5211/32]$; H, $(4s)-[31]$.

(D) C, $[9s5p]$ uncontracted; H, $(4s)-[22]$ (best for C).

(E) C, $(9s5p)-[5211/32]$; H, $[4s]$ uncontracted (best for H).

−25.7 G for hydrogen. Among the $[4s2p/2s]$ contracted basis sets (A), (B), and (C), the contraction (A) gives the best hfs result in comparison with the uncontracted result, though it gives the worst energy. The contraction type [5211/32] on carbon, which was first used by Ellinger *et al.*,[6(b)] and [22] on hydrogen, i.e., the contraction (A), seems to give more variational flexibility in the vicinity of the nucleus than the contraction type [6111/41] on carbon and [31] on hydrogen originally due to Dunning.[22] The type (A) contraction for the atoms H, C, N, O, and F are listed in Table III.

TABLE III. Contracted Gaussian basis set used in the present calculation [type (A) in Table II].

Exponents	Coefficients	Exponents	Coefficients
Carbon s set		Nitrogen s set	
4232.6100	0.002336	5909.4400	0.002313
634.8820	0.017884	887.4510	0.017670
146.0970	0.086818	204.7490	0.085745
42.4974	0.298521	59.8376	0.292420
14.1892	0.686791	19.9981	0.693154
5.1477	0.772924	7.1927	0.777532
1.9666	0.257253	2.6859	0.253646
0.4962	1.000000	0.7000	1.000000
0.1533	1.000000	0.2132	1.000000
Carbon p set		Nitrogen p set	
18.1557	0.039196	26.7860	0.038244
3.9864	0.244143	5.9564	0.243846
1.1429	0.816773	1.7074	0.817192
0.3594	0.668140	0.5314	0.669566
0.1146	0.417933	0.1654	0.419782
Oxygen s set		Fluorine s set	
7816.5400	0.002328	9994.7900	0.002315
1175.8200	0.017696	1506.0300	0.017550
273.1880	0.084571	350.2690	0.083893
81.1696	0.283858	104.0530	0.282762
27.1836	0.701408	34.8432	0.702937
9.5322	0.791812	12.2164	0.791631
3.4136	0.240562	4.3689	0.240848
0.9398	1.000000	1.2078	1.000000
0.2846	1.000000	0.3634	1.000000
Oxygen p set		Fluorine p set	
35.1832	0.040023	44.3555	0.042011
7.9040	0.253849	10.0820	0.261899
0.2305	0.806841	2.9959	0.797663
0.7171	0.652812	0.9383	0.644783
0.2137	0.444296	0.2733	0.456370
Hydrogen s set			
13.3615	0.130844		
2.0133	0.921539		
0.4538	0.516820		
0.1233	0.554495		

TABLE IV. ζ_H dependence of hfs constants (in G) of CH_3 and CH_3CH_2.[a]

	ζ_H 1.0	ζ_H 1.2	ζ_H 1.4	Exptl.
CH_3				
a(C)	38.4	39.4	38.7	38.3
a(H)	−25.7	−26.5	−27.8	−23.0
Energy (a.u.)	−39.5211	−39.5451	−39.5543	
CH_3CH_2				
$a_{SD}(H_\beta)$	10.6	10.9	11.7	
$a_{SP}(H_\beta)$	9.1	9.2	9.5	
$a(H_\beta)$	19.7	20.1	21.2	26.9
Energy (a.u.)	−78.5232	−78.5585	−78.5709	

[a]Results of the pseudo-orbital theory.

The hfs constant of hydrogen depends surprisingly little on the change in the scale factor ζ_H.[6(b)] This is shown in Table IV for methyl and ethyl radicals. Both the SD and SP contributions are insensitive to ζ_H. Thus, we have used the value $\zeta_H = 1.2$ from the energetic point of view.

The effect of polarization functions was also examined. The effect of the p function on hydrogen was very small and the effect of the d function on carbon was also not large (Table V). Then, for practical use, we have not included any polarization functions in the following calculations of hfs constants.

In the results of Ellinger *et al.*, shown in Table I, the uses of the canonical orbitals and quasilocalized orbitals give largely different values. This is due to the fact that the first-order perturbation theory depends largely on the unitary transformations among the reference molecular orbitals. This fact is not preferable from the theoretical point of view, and can be corrected by completely diagonalizing the secular equation, i.e., by including the (off-diagonal) coupling terms.[14]

In Table I, we have summarized the present results obtained by the pseudo-orbital (PO) theory, and the UHF,

TABLE V. Effect of polarization functions in CH_3.[a]

Basis set	a(C) (G)	a(H) (G)	Energy (a.u.)
$[4s2p/2s]$	39.4	−26.5	−39.5451
$[4s2p/2s1p]$[b]	38.9	−26.2	−39.5512
$[4s2p1d/2s]$ $\alpha_d(C) = 0.3852$	35.8	−24.6	−39.5592

[a]Results of the pseudo-orbital theory.

[b]The p function on hydrogen is 2-GTO ($\alpha_1 = 13.3615$, $\alpha_2 = 2.0133$; $c_1 = 0.13378$, $c_2 = 0.94225$).

TABLE VI. Molecular geometry used for the present calculation.

Molecule	Structure	Reference
CH_3	CH = 1.079 Å	20
CH_3CH_2	CC = 1.498 Å, CH_α = 1.076 Å CH_β = 1.090 Å, CH_β' = 1.086 Å CCH_β = 112.01°, CCH_β' = 111.42° $H_\alpha C_\alpha H_\alpha$ = 118.38°, CCH_α = 120.6°	26
CH_2CHCH_2	CC = 1.40 Å, CH = 1.08 Å, CCC = CCH = HCH = 120°	
NH_2	NH = 1.024 Å, HNH = 103.4°	20
NF_2	NF = 1.37 Å, FNF = 104.2°	20
O_3^-	OO = 1.19 Å, OOO = 100°	27
CH_2CH	CC = 1.34 Å, CH = 1.08 Å HCH = 120°, CCH = 138°	6
cyclo-C_3H_5	CC = 1.524 Å, CH = 1.07 Å HCH = 120°, CCC = 60°, CCH_α = 41°	6
HCO	CO = 1.19 Å, CH = 1.08 Å, HCO = 119.5°	20
NO_2	NO = 1.1934 Å, ONO = 134.1°	20

PUHF, and the SECI theories with the same [4s2p/2s] basis set. The PO theory has given 39.4 G for carbon and −26.5 G for hydrogen, in good agreement with experiment. The UHF value is too large to compare with the experimental value, while the PUHF value, which is one third of the UHF value as proved theoretically,[10] is too small. The differences between the PO and SECI values show the spin-polarization self-consistency effect included to first order in the present calculation. It is about 2 G for hydrogen and about 6 G for carbon, which is relatively small in comparison with the previous results for atoms.[16] We also see the following inequality as proved previously[11,16]:

$$|\rho_{SP}^{SECI}| < |\rho_{SP}^{PO}| < |\rho_{SP}^{UHF}| \tag{17}$$

IV. GENERAL RESULTS AND DISCUSSIONS

The hfs constants of π radicals (methyl, ethyl, allyl, NH_2, O_3^- and NF_2) are calculated by the UHF, PUHF, SECI, and PO theories. (The geometries are listed in Table VI.) The results are shown in Table VII. In π radicals, the unpaired spin orbital has a node on the molecular plane so that the a_{SD} term does not contribute to the hfs constants of the nuclei lying on the molecular plane. Thus, for π radicals, it is particularly important to correctly take into account the spin-correlation effect.

The hfs constants calculated by the UHF theory are always much larger than the experimental values for nuclei on the molecular plane. The PUHF results satisfy the relation derived previously[10,11] to a good extent:

$$(\rho_{SP})_{UHF} \cong \frac{s+2}{s} (\rho_{SP})_{PUHF} , \tag{18}$$

where $s = 1, 2, \ldots$ for doublet, triplet, etc. They are, however, too small to compare with the experimental values. The PO and SECI theories give better agreement with experiments. The spin-polarization self-consistency effect included to first order in the present PO calculation is relatively large for first-row atoms at the radical center. The relation (17) holds for calculated values without exceptions. In comparison with the results of Ellinger *et al.*, the independence of the unitary transformations among occupied or virtual orbitals seems to be important to obtain consistent agreement with experiment.

Next we compare in more detail the PO and SECI results with experiment. The hfs constant for methyl and allyl radicals are in satisfactory agreement with the experimental results. In the case of allyl radical, the calculated hfs constant of proton H_3 is a little larger than that of proton H_4. This result is consistent with the experimental result. For ethyl radical, the hfs constants are in good agreement with the experimental val-

TABLE VII. Hyperfine splitting constants of π radicals (G).

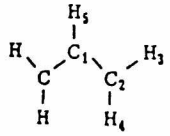
Molecule	Nucleus	UHF	PUHF	Pseudo-orbital	SECI	Exptl.	(Ref.)
CH_3	C	71.3	24.8	39.4	33.3	38.3	[25(a)]
	H	−40.6	−13.2	−26.5	−24.3	−23.0	
$CH_3\dot{C}H_2$	$\dot{C}$	76.4	28.1	45.1	38.7	39.1	
	C	−28.4	−9.3	−18.3	−16.1	−13.6	[25 (a), (b)]
	H_α	−39.6	−12.8	−26.0	−23.8	−22.4	
	H_β	24.6	15.7	20.1	19.6	26.9	
	C_1	−68.2	−22.1	−25.2	−21.8	···	
	C_2	65.7	22.8	26.4	22.0	···	
	H_3	−32.7	−10.7	−15.8	−14.0	−14.8	(28)
	H_4	−32.2	−10.6	−15.4	−13.7	−13.9	
	H_5	21.9	7.4	3.8	2.0	4.1	
NH_2	N	15.0	5.2	7.4	6.4	10.3	[29(b)]
	H	−36.3	−11.9	−24.2	−21.9	−23.9	
NF_2	N	20.2	7.1	12.7	11.8	17	(30)
	F	118.1	40.4	77.2	69.7	60	
	O_1	−40.6	−13.8	−26.2	−23.9	−22.2	(31)
	O_2	−19.3	−6.5	−12.4	−11.3	−10.5	

TABLE VIII. Hyperfine splitting constants of σ radicals (G).

Molecule	Nucleus	UHF			PUHF			Pseudo-orbital			SECI			Expt.	(Ref.)
		a_{SD}	a_{SP}	a	a_{SD}	a_{SP}	a	a_{SD}	a_{SP}	a	a_{SD}	a_{SP}	a		
$H_4 \diagdown C_2 - C_1^{\cdot} \diagup H_3$ $H_5 \diagup$	C_1	117.7	88.6	206.3	117.7	29.5	147.2	119.4	23.0	142.4	121.3	19.0	140.4	107.6	
	C_2	8.9	−74.5	−65.7	8.9	−24.2	−15.3	9.5	−23.2	−13.7	9.7	−19.1	−9.4	−8.6	
	H_3	19.3	−36.5	−17.2	19.3	−12.2	7.1	23.5	−12.4	11.1	23.9	−10.4	13.5	13.3	[25(a), (b)]
	H_4	13.0	36.6	49.6	13.0	12.2	25.2	12.9	11.5	24.4	13.1	9.4	22.6	34.2	
	H_5	21.5	14.9	66.4	21.5	15.0	36.5	21.8	17.5	39.3	22.2	15.2	37.4	68.5	
	C_1	121.8	56.5	178.3	121.8	18.8	140.6	122.2	31.0	153.2	122.2	26.6	148.8	...	
	C_2	2.3	−18.1	−15.8	2.3	−6.0	−3.7	2.2	−10.5	−8.3	2.2	−9.1	−6.9	...	
	H_3	14.1	−26.5	−12.4	14.1	−8.8	5.3	15.0	−16.2	−1.3	15.0	−14.7	0.3	−6.5	(24),
	H_4	8.9	9.4	18.3	8.9	3.1	12.0	8.6	6.6	15.1	8.6	5.9	14.5	larger (23.4)	[25(b)], (33)
	H_5	6.8	6.9	13.7	6.8	2.3	9.1	6.7	4.4	11.1	6.7	3.8	10.5	smaller	
$O - C^{\cdot} \diagdown H$	C	157.8	18.8	167.6	157.8	6.3	164.1	154.8	4.4	159.1	154.8	4.6	159.4	134.5	
	H	86.4	28.4	114.8	86.4	9.5	95.9	84.7	24.5	109.2	84.7	23.9	108.6	136.5	[29(a)]
	O	−4.5	−10.3	−14.8	−4.5	−3.4	−7.9	−3.9	−10.2	−14.1	−3.9	−9.7	−13.6	...	
NO_2	N	44.2	−0.7	43.5	44.2	−0.2	44.0	43.3	−0.8	42.5	43.3	−1.1	42.2	52.3	
	O	−7.3	−2.8	−10.1	−7.3	−0.9	−8.2	−5.8	−3.3	−9.1	−5.8	−2.6	−8.4	...	(32)

ues except for the β proton, for which the calculated value 20.1 G, which is obtained assuming free rotation, is rather small compared to the experimental value of 26.9 G. For the hfs value of this β proton, the geometry dependence was found to be large. In our calculation, the hfs value increased about 6 G when the C–C length was shortened by 0.1 Å. Note that the SP contribution is comparable to the SD contribution for the β-proton hfs constant as seen in Table IV. The $\cos^2\theta$ dependence of the SP contribution has been shown previously.[23] For the hfs constants of the nuclei N, O, and F of NH_2, O_3^-, and NF_2 radicals, respectively, we have also obtained satisfactory results in comparison with experimental values.

Table VIII shows the results for σ radicals. The hfs constants are the sums of the SD and SP contributions. The SD and SP contributions in the UHF and PUHF theories are calculated using the previous formulas[10,11]:

$$(\rho_{UHF})_{SP} = \tfrac{1}{2}s[1 + (2/s)](\rho_{UHF} - \rho_{PUHF}) \ ,$$

$$(\rho_{PUHF})_{SP} = \tfrac{1}{2}s(\rho_{UHF} - \rho_{PUHF}) \ ,$$

$$(\rho)_{SD} = \rho - (\rho)_{SP} \ . \qquad (19)$$

Also, for σ radicals, the UHF values seem to be consistently larger than the experimental values. This is due to the failure in the SP contribution. Therefore, the UHF theory does not explain the *positive* hfs constant of H_3 nucleus of vinyl radical. Though the PUHF theory does give a positive value for this hfs constant, it does not explain the *negative* hfs constant of the H_3 nucleus of cyclopropyl radical. The results of the PO and SECI theory are close. However, among these theories, *only* the PO theory is successful in explaining the *different* signs of the α-proton (H_3) hfs constants of vinyl and cyclopropyl radicals.

Next, we compare in more detail the PO and SECI results with the experimental values. For vinyl radical, the hfs constant of β proton H_5, *trans* to the radical lobe is calculated to be larger than that of the *cis* β proton H_4. For cyclopropyl radical, however, the calculated hfs constants of β protons show the opposite relation to vinyl radical. This fact has been confirmed experimentally.[24] For vinyl and cyclopropyl radicals, the SP contributions to α-proton hfs constants are negative, but different relative contributions between a_{SD} and a_{SP} terms result in positive and negative hfs constants for vinyl and cyclopropyl radicals, respectively. Only the PO theory gives correct signs for both radicals. On the other hand, the a_{SP} term of the α proton of formyl radical is a large *positive* value of 24.5 G and adds up to a large a_{SD} term of 84.7 G. This is one of the reasons that the large hfs constant has been observed for the α proton of formyl radical.

V. CONCLUSIONS

In this paper, the hfs constants of various σ and π radicals which contain H, C, N, O, and F nuclei are calculated with the UHF, PUHF, SECI, and pseudo-orbital (PO) theories. The basis sets are examined to give good hfs constants. The [5211/32] contraction of Huzinaga's (9s5p) basis of first-row atoms and [22] con-

traction of hydrogen (4s) basis are adopted. Within the range examined here (changes in contraction, addition of p- or d-polarization functions, and variations in the scale factor ζ_H), the basis set dependence was small. On the other hand, the calculated hfs constants depend strongly on the theory used. The UHF theory gives consistently too large values to compare with experiments, while the PUHF values were too small. The reason for this failure is already clear.[11,16] The PO and SECI theories have given fairly good agreements with experiment. For molecules studied here, the spin-polarization self-consistency effect, which is included to first order in the present PO calculation but is absent in the SECI theory, was relatively small in contrast to the previous results for atoms.[16] It was about 6 G for a_C and 2 G for a_H of methyl radical. A comparison with the results of the first-order perturbation theory due to Ellinger *et al.*[6] implies an importance of eliminating the orbital unitary transformation dependence to obtain consistent agreement with experiment. The present results with the PO and SECI theories have well explained several important variations in the experimental hfs constants of organic and inorganic σ and π radicals.

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[1]W. A. Goddard, Phys. Rev. 157, 93 (1967); 182, 48 (1967).
[2]H. F. Schaefer, R. A. Klemm, and F. E. Harris, Phys. Rev. 176, 49 (1968); 181, 137 (1969).
[3]W. Meyer, J. Chem. Phys. 51, 5149 (1969).
[4]S. Y. Chang, E. R. Davidson, and G. Vincow, J. Chem. Phys. 52, 1740 (1970).
[5]H. Konishi and K. Morokuma, J. Am. Chem. Soc. 94, 5603 (1972).
[6](a) P. Millie, B. Levy, and G. Berthier, Int. J. Quantum Chem. 6, 155 (1972); (b) Y. Ellinger, A. Rassat, R. Subra, and G. Berthier, J. Chem. Phys. 62, 1 (1975); (c) Y. Ellinger, R. Subra, B. Levy, P. Millie, and G. Berthier, *ibid.* 62, 10 (1975); (d) Y. Ellinger, R. Subra, and G. Berthier, J. Am. Chem. Soc. 100, 4061 (1978).
[7]D. M. Chipman, J. Chem. Phys. 71, 761 (1979).
[8]J. A. Pople and R. K. Nesbet, J. Chem. Phys. 22, 571 (1954).
[9]P.-O. Löwdin, Phys. Rev. 97, 1490, 1509 (1955); R. Pauncz, *Alternant Molecular Orbital Method* (Saunders, Philadelphia, 1967); K. M. Sando and J. E. Harriman, J. Chem. Phys. 47, 180 (1967); U. Kaldor, J. Chem. Phys. 48, 835 (1968).
[10]H. Nakatsuji, H. Kato, and T. Yonezawa, J. Chem. Phys. 51, 3175 (1969).
[11]H. Nakatsuji, J. Chem. Phys. 59, 2586 (1973).
[12]W. A. Goddard, J. Chem. Phys. 48, 1008 (1968).
[13]K. Hirao and H. Nakatsuji, J. Chem. Phys. 69, 4535, 4548 (1978).
[14]H. Nakatsuji, J. Chem. Phys. 61, 3278 (1974).
[15]H. Nakatsuji and K. Hirao, J. Chem. Phys. 68, 2053 (1978).
[16](a) H. Nakatsuji and K. Hirao, Chem. Phys. Lett. 47, 569 (1977); (b) H. Nakatsuji and K. Hirao, J. Chem. Phys. 68, 4279 (1978).
[17]D. J. Thouless, Nucl. Phys. 21, 225 (1960).
[18]C. C. J. Roothaan, Rev. Mod. Phys. 32, 179 (1960).
[19]T. Yonezawa, H. Nakatsuji, T. Kawamura, and H. Kato, J. Chem. Phys. 51, 669 (1969).
[20]G. Herzberg, *Electronic Spectra of Polyatomic Molecules* (Van Nostrand, Princeton, 1967).
[21]S. Huzinaga, J. Chem. Phys. 42, 1293 (1965).
[22]T. H. Dunning, J. Chem. Phys. 53, 2823 (1970).
[23]H. Nakatsuji, H. Kato, and T. Yonezawa, Bull. Chem. Soc. Jpn. 43, 698 (1970).
[24]T. Kawamura, M. Tsumura, Y. Yokomichi, and T. Yonezawa, J. Am. Chem. Soc. 99, 8251 (1977).
[25](a) R. W. Fessenden, J. Phys. Chem. 71, 74 (1967); (b) R. W. Fessenden and R. H. Schuler, J. Chem. Phys. 39, 2147 (1963); (c) 43, 2704 (1965).
[26]J. Pacansky and M. Dupuis, J. Chem. Phys. 68, 4276 (1978).
[27]L. V. Azaroff and I. Corvin, Proc. Natl. Acad. Sci. U.S.A. 49, 1 (1963).
[28]J. K. Kochi and P. J. Krusic, J. Am. Chem. Soc. 90, 7157 (1968).
[29](a) E. L. Cochran, F. J. Adrian, and V. A. Bowers, J. Chem. Phys. 44, 4626 (1966); (b) S. Foner, E. L. Cochran, V. A. Bowers, and C. Jen, Phys. Rev. Lett. 1, 91 (1958).
[30]J. B. Farmer, M. C. L. Gerry, and C. A. McDowell, Mol. Phys. 8, 253 (1964).
[31]S. Schlick, J. Chem. Phys. 56, 654 (1972).
[32]G. R. Bird, J. C. Bird, A. W. Jache, J. A. Hodgeson, R. F. Curl, Jr., A. C. Kunkle, J. W. Bransford, J. R. Anderson, and J. Rosenthal, J. Chem. Phys. 40, 3378 (1964).
[33]The sign is reported as negative for the α proton of the cyclopropyl radical: R. Kaptain, *Chemically Induced Magnetic Polarization*, edited by A. R. Lepley and G. L. Closs (Wiley, New York, 1973), Chap. 4.

PART I, Chapter 3

Self-Consistency in the Pseudo-Orbital Theory and the Spin Correlations of Doublet Radicals

I. INTRODUCTION

Spin correlation problem has been studied extensively through the calculation of spin densities which are observed directly from hyperfine splitting (hfs) constants of E.S.R spectra. Most of the calculations have been carried out within the conventional open-shell orbital theories such as the unrestricted Hartree Fock (UHF) theory[1]. The UHF wavefunction is, however, not adapted to the spin symmetry and it always gives too large spin densities to comapre with experiments[2]. Spin-extended UHF (SEHF)[3] theory is constructed to adapt the spin symmetry. However it can not cure the incorrect self-consistency in the UHF theory and they do not give reasonable results for both of the spin and electron correlation problems[4b]. Pseudo-orbital (PO) theory[4] is a new open-shell orbital theory and it includes only one-electron excitations within symmetry-adapted-cluster (SAC) expansion theory[4b]. The PO theory considers the spin correlation effect adequately. and is free from the theoretical defects in the conventional open-shell orbital theories. In the previous work[5], the PO theory was applied to various σ and π radicals. We used there the linearized variational equation[4b] of the PO theory and calculated spin densities up to second order in the variational coefficients. Calculated spin densities were in fair agreement with the experimental results and much better than that of the UHF theory. At the nuclei which are distant from the center of radical, however, rather small hfs constants were calculated in comparison with experimental values. For example, the hfs constant at the β -proton of ethyl radical was 20.1G compared

with the experimental value, 26.9G[6]. Coupling with the electron correlation effect is thought to be one of the important factors to improve this result. In the previous work[7], we calculated spin densities by the SAC and SAC-CI theories considering the spin and electron correlations at the same time and obtained fairly improved value, 22.4G, for hfs constants at the β-protons. Another important factor to be examined is a self-consistency or higher order effect of the spin correlation within the PO theory. It was not considered in the previous works because of the linearized variational equation. It is an aim of this study to examine this self-consistency effect by using a iterative natural orbital technique. Excitation operators which contribute to the spin delocalizatin are also considered though they are not so important from the energetical point of view.

Calculational details are given in the next section. Results and discussions are in Sec.III and conclusions of this study is in Sec.IV, respectively.

II. METHOD OF CALCULATION

The self consistency effect of the PO theory was taken into account by solving the linearized variational equation iteratively with the use of natural orbitals.

The wavefunction of the PO theory is written for the (2s+1) spin multiplicity as,

$$\Psi_{PO}^{2s+1} = \mathcal{A} \exp\left(\sum_I C_I S_I^+\right) |0\rangle, \tag{1}$$

$$|0\rangle = ||\phi_1\bar{\phi}_1 \cdots \phi_i\bar{\phi}_i \cdots \phi_q\bar{\phi}_q\phi_{q+1} \cdots \phi_p||, \; s = p - q. \tag{2}$$

where s is the number of unpaired electrons and $\mathcal{P}$ is a symmetry projector. $|0\rangle$ is a reference configuration and we use the open-shell restricted HF (RHF) wavefunction. C_I is a variational coefficient of a symmetry-adapted excitation operator S_I^+.

Here we considered ${}^{P}S_i^{a+}$, ${}^{0}S_i^{a+}$, ${}^{0}S_i^{m+}$, and ${}^{0}S_m^{a+}$ operators. The suffix i means a doubly occupied orbital, suffix m is a singly occupied orbital, and suffix a is a virtual orbital in the reference configuration. Explicit form of these four linked operators are written using the creation and anihilation operators of fermion as follows,

$$ {}^{P}S_i^{a+} = (s+1)^{-1/2}[(s/2)^{1/2}(a^+_{a\alpha}a_{i\alpha} - a^+_{a\beta}a_{i\beta}) + (2/s)^{1/2}a^+_{a\alpha}a_{i\beta}\sum_{m=q+1}^{p} a^+_{m\beta}a_{m\alpha}], \quad (3a) $$

$$ {}^{0}S_i^{a+} = (1/2)^{1/2}(a^+_{a\alpha}a_{i\alpha} + a^+_{a\beta}a_{i\beta}), \quad (3b) $$

$$ {}^{0}S_i^{m+} = a^+_{m\beta}a_{i\beta}, \quad (3c) $$

$$ {}^{0}S_m^{a+} = a^+_{a\alpha}a_{m\alpha}. \quad (3d) $$

${}^{P}S_i^{a+}$ is a spin-polarization operator and plays a dominant role in the spin correlation. ${}^{0}S_i^{a+}$, ${}^{0}S_i^{m+}$, and ${}^{0}S_m^{a+}$ operators do not contribute in first order since they satisfy the Brillouin theorem for the RHF wavefunction. The linearized variational equation which retaining terms up to first order in the variational coefficients is,

$$ \langle 0|HS_I^+|0\rangle + \sum_J C_J(\langle 0|S_JHS_I^+|0\rangle + \langle 0|HS_I^+S_J^+|0\rangle - \delta_{IJ}E) = 0, \quad (4) $$

for all I included in Eq.(1). The third term is an unlinked effect introduced by the PO theory. Here we try to introduce higher unlinked terms of S_I^+ by solving Eq.(4) iteratively with natural orbitals. First we solve the Eq.(4) and calculate the

approximate natural orbitals from the solution vector. Next we solve the Eq.(4) again constructing the reference configuration with the approximate natural orbitals. These procedures were carried out iteratively.

Spin density and charge density matrices were calculated up to second order in the variational coefficients.

$$\bar{\rho}(r) = N[\langle 0|\hat{\rho}(r)|0\rangle + 2\sum_I C_I \langle 0|S_I \hat{\rho}(r)|0\rangle + \sum_I \sum_J C_I C_I \langle 0|S_I \hat{\rho}(r) S_J^+|0\rangle], \quad (5)$$

where $\bar{\rho}(r)$ is a spin density or charge density operator defined

$$\hat{\rho}_{spin}(r) = 2\sum_\nu S_z(\nu)\delta(r-r_\nu), \quad (6a)$$

$$\hat{\rho}_{charge}(r) = \sum_\nu \delta(r-r_\nu). \quad (6b)$$

The first-order terms of the spin density matrix are represented in the orbital basis as follows,

$$\langle 0|\hat{\rho}_{spin}(r)\,{}^P S_i^{a+}|0\rangle = [2s/(s+2)]^{1/2}\rho_{ia}(r), \quad (7a)$$

$$\langle 0|\hat{\rho}_{spin}(r)\,{}^0 S_i^{a+}|0\rangle = 0, \quad (7b)$$

$$\langle 0|\hat{\rho}_{spin}(r)\,{}^0 S_i^{m+}|0\rangle = -\rho_{im}(r), \quad (7c)$$

$$\langle 0|\hat{\rho}_{spin}(r)\,{}^0 S_m^{a+}|0\rangle = \rho_{ma}(r),$$

and for the charge density matrix,

$$\langle 0|\hat{\rho}_{charge}(r)\,{}^P S_i^{a+}|0\rangle = 0, \quad (8a)$$

$$\langle 0|\hat{\rho}_{charge}(r)\,{}^0 S_i^{a+}|0\rangle = (1/2)^{1/2}\rho_{ia}(r), \quad (8b)$$

$$\langle 0|\hat{\rho}_{charge}(r)\,{}^0 S_i^{m+}|0\rangle = \rho_{im}(r), \quad (8c)$$

$$\langle 0|\hat{\rho}_{charge}(r)\,{}^0 S_m^{a+}|0\rangle = \rho_{am}(r), \quad (8d)$$

where $\rho_{ij}(r)=\phi_i(r)^*\phi_j(r)$.

The ${}^P S_i^{a+}$ contributes in the first order to the spin density as shown in Eq.(7a) and does not contribute to charge density as in Eq.(8a). Then the ${}^P S_i^{a+}$ operator can not create the approximate natural orbital by itself. On the other hand, ${}^0 S_i^{a+}$ contribute to charge density matrix in the first order though

its variational coefficient is small due to the Brillouin theorem for RHF wavefunction. ${}^{0}S_{i}^{m+}$ and ${}^{0}S_{m}^{a+}$ contribute to spin and charge density matrices and relax the open-shell orbital though their expansion coefficients are also small due to the Brillouin theorem.

In the test calculation, we studied ethyl radical in doublet ground state. The hfs constants at the β -proton was calculated rather small in the previous study[5] using the linearized variational equation. The basis set is Huzinaga's[8] (9s5p/4s) GTO contracted to [4s2p/2s] with the scale factor of hydrogen, 1.2, as in the previous work[5]. Molecular geometry is fixed to the optimized geometry by the UHF wavefunction[9].

III. RESULTS AND DISCUSSION

In Table I, calculated energies and hfs constants are shown. The energy of the second iteration which considered only the ${}^{P}S_{i}^{a+}$ operator is slightly lower than that of the first iteration. Spin densities, however, did not changed. The calculations which considered only one of the ${}^{0}S_{i}^{a+}$, ${}^{0}S_{i}^{m+}$, and ${}^{0}S_{m}^{a+}$ operators gave the same hfs constants in the open-shell RHF wavefunction since they do not polarize spin density in first order. The coupling of ${}^{P}S_{i}^{a+}$ and other operators have been also studied. Obtained energy were slightly lower than the solution of S alone. Iterative natural orbital technique was used for the calculation which considered ${}^{P}S_{i}^{a+}$ and ${}^{0}S_{i}^{a+}$, or ${}^{P}S_{i}^{a+}$ and ${}^{0}S_{m}^{a+}$ operators. Both of the energy and hfs constants did not change. From these results, the higher order effects, which is

introduced by the iterative natural orbital technique, is found to be already incorporated enough in the linearized variational equation if we use the RHF wavefunction as a reference configuration. Then, in order to improve the spin correlation, it is thought to be important that the non-linear variational equation should be solved directly.

IV. CONCLUSION

The self consistency effect of the PO theory has been studied by the iterative natural orbital technique. Obtained energies and hfs constants for ethyl radical did not change from the previous result[5]. This means that the self-consistency effect which is introduced by this iterative technique is already incorporated enough in the linearized variational equation if the molecular orbitals of RHF are used in the reference configuration. The effect of ${}^{0}S_{i}^{m+}$ and ${}^{0}S_{m}^{a+}$ which were expected to contribute to the spin delocalization directly did not so effective because their expansion coefficients were small due to the Brillouin theorem and the iteration by natural orbitals did not improve their contribution in first order. From the above results, it is thought to be important for the improved spin correlations that the non-linear variational equation should be solved directly considering the coupling effects.

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References

1. J.A.Pople and R.K.Nesbet, J.Chem.Phys. 22, 571 (1954).

2. (a) H.Nakatsuji, H.Kato, and T.Yonezawa, J.Chem.Phys. 51, 3175 (1969). (b) H.Nakatsuji, J.Chem.Phys. 59, 2586 (1973).

3. P.-O.Lowdin, Phys.Rev. 97, 1490, 1509 (1955); R.Pauncz, Alternant Molecular Orbital Method (Saunders, Philadelphia); K.M.Sando and J.E.Harriman, J.Chem.Phys. 47, 180 (1967); U.Kaldor, J.Chem.Phys. 48, 835 (1968).

4. (a) H.Nakatsuji and K.Hirao, Chem.Phys.Lett. 47, 569 (1977). (b) H.Nakatsuji and K.Hirao, J.Chem.Phys. 68, 2053, 4279 (1978).

5. K.Ohta, H.Nakatsuji, K.Hirao, and T.Yonezawa, J.Chem.Phys. 73, 1770 (1980).

6. R.W.Fessenden, J.Phys.Chem. 71, 74 (1967); R.W.Fessenden and R.H.Schuler, J.Chem.Phys. 39, 2147 (1963).

7. H.Nakatsuji, K.Ohta, and T.Yonezawa, to be published.

8. S.Huzinaga, J.Chem.Phys. 42, 1293 (1965).

9. J.Pacansky and M.Dupuis, J.Chem.Phys. 68, 4276 (1978).

Table I. Electronic energy and hfs constants of ethyl radical[a].

Operator	Iteration	E(a.u.)	hfs (gauss)			
			C_β	C_α	H_β	H_α
$P_{S_i^{a+}}$	1	-115.531902	-18.24	45.17	20.59	-26.01
	2	-115.531910	-18.24	45.15	20.59	-26.01
$^0S_i^{a+}$	1	-115.523324	0.11	2.56	11.37	0.21
$^0S_i^{m+}$	1	-115.523324	0.11	2.56	11.37	0.21
$^0S_m^{a+}$	1	-115.523324	0.11	2.56	11.37	0.21
$P_{S_i^{a+}{}^0S_i^{m+}}$	1	-115.532015	-18.27	45.24	19.15	-26.03
$P_{S_i^{a+}{}^0S_i^{a+}}$	1	-115.531915	-18.28	45.39	20.59	-26.05
	2	-115.531918	-18.28	44.99	20.60	-26.06
$P_{S_i^{a+}{}^0S_m^{a+}}$	1	-115.531924	-18.34	46.00	20.91	-26.08
	2	-115.531948	-18.38	44.89	20.93	-26.09
	3	-115.531949	-18.38	44.89	20.93	-26.09
$P_{S_i^{a+}{}^0S_i^{m+}{}^0S_m^{a+}}$	1	-115.532041	-18.36	44.90	19.37	-26.12
$P_{S_i^{a+}{}^0S_i^{a+}{}^0S_i^{m+}{}^0S_m^{a+}}$	1	-115.532056	-18.40	45.11	19.35	-26.15
Exptl.[b]		----------	-13.6	39.1	26.9	-22.4

a: Electronic energy is -115.523031 a.u. by the open-shell RHF theory.
b: Reference 6.

CHAPTER 4

SUMMARY

In chapter 2, the spin correlation in the PO theory has been investigated by the calculation of hyperfine splitting constants (hfsc) of methyl, ethyl, vinyl, allyl, cyclopropyl, formyl, O_2, NH_2, NO_2, and NF_2 radicals. The PO wavefunction was obtained by diagonalizing the linearized variational equation completely. Calculated spin densities were compared with the results of experiments and of the conventional orbital theories, such as the UHF or anihilated UHF (AUHF) theories. The UHF results were consistently too large to compare with experiments and the AUHF results were too small. On the other hand, the PO theory gave fairly good results and explained well several important variations in the experimental hfsc's. In chapter 3, the higher order effect of spin polarization operators has been studied by iterative natural orbital technique. The operators which contribute to spin delocalization directly were also considered. Obtained results, however, did not changed from the result of the PO theory of the linearized variational equation. This means that the self-consistency effect which is incorporated by the iterative natural orbitals is already considered enough in the linearized variational equation if the HF orbitals are used in the reference configuration.

PART II

SPIN AND ELECTRON CORRELATIONS OF DOUBLET RADICALS STUDIED BY THE SYMMETRY-ADAPTED-CLUSTER (SAC) AND SAC-CI THEORIES

CHAPTER 1

INTRODUCTION

In Part I of this thesis, spin correlation problems have been studied by the pseudo-orbital (PO) theory. It containes only the one electron symmetry-adapted excitation operators and does not consider electron correlation effects. For the electron correlation problems, linked operators which correlate two particles and their unlinked terms are known to play a dominant role by Sinanoglu's meny electron theory (MET)[1]. The cluster expansion theory based on his study converges faster than the conventional linear expansion theory, such as configuration interaction (CI) theory, and satisfy the size-consistency effect of the correlation energy. Recently, the cluster expansion theory has been generalized and extended to open-shell systems as symmetry-adapted-cluster (SAC) theory by Nakatsuji and Hirao[2a]. Wavefunction of excited states have been also constructed by the SAC-CI theory[2b,c]. The SAC-CI wavefunction is orthogonal and orthogonal with respect to the hamiltonian with the ground state SAC wavefunction and satisfies the necessary conditions of the wavefunction for excited states. In chapter 2, we studied the spin and electron correlations at the same time by these theories in various doublet radicals. There are few studies[3] which calculate spin densities and correlation energies in molecules at the same time. Coupling effect of these two correlations are also discussed. Chapter 3 gives the theoretical study for the vertical excitation, ionization energies, and spin densities of NO_2 radical by the SAC and SAC-CI wavefunctions. NO_2 is one of the stable free

radicals and the electron correlation effect is known to be important in ground and excited states[4].

References

1. O.Sinanoglu, J.Chem.Phys. 36, 706, 3198 (1962).

2. (a) H.Nakatsuji and K.Hirao, J.Chem.Phys. 68, 2053, 4279 (1978). (b) H.Nakatsuji, Chem.Phys.Lett. 59, 362 (1978). (c) H.Nakatsuji, Chem.Phys.Lett. 67, 329, 334 (1979).

3.(a) C.F.Bender and E.R.Davidson, Phys.Rev. 183, 292 (1969); (b) S.Y.Chang, E.R.Davidson, and G.Vincow, J.Chem.Phys. 52, 1740 (1970); (c) C.F.Jackels and E.R.Davidson, J.Chem.Phys. 63, 4672 (1975). (d) J.E.Rodgers, T.Lee, T.P.Das, and D.Ikenberry, Phys.Rev. A7, 51 (1973); J.E.Rodgers and T.P.Das, Phys.Rev. A8, 2195 (1973).

4. C.F.Jackels and E.R.Davidson, J.Chem.Phys. 64, 2908 (1976).

PART II, Chapter 2

Spin and Electron Correlations in BeH, NH_2, CH_3, CH_2CH, CH_3CH_2, and HCO Radicals

1. INTRODUCTION

In this series of studies,[1-5] we are developing SAC (symmetry-adapted-cluster) and SAC-CI theories applied to the studies of the electron correlations in the ground and various excited states of molecules. So far, this theory has been applied successfully to the ground state and the singlet and triplet excited states, ionized states, and electron attached states,[3-4] which are essentially one-electron excitation processes, and to the states involved in the satellite peaks of the inner-valence ionization,[5] which are essentially two-electron excitations from the Hartree-Fock reference state.[6]

In the previous works[7], we studied spin correlations in open-shell atoms and molecules by the pseudo-orbital (PO) theory which includes only one-electron spin-polarization excitation operators in the framework of the SAC theory. In this study we apply the SAC and SAC-CI theories to the doublet radicals, BeH, NH_2, CH_3, CH_2CH, CH_3CH_2, and HCO, considering not only spin correlations but also electron correlations. Though there are many works for atoms which studied electron correlations and spin correlations at the same time by the Brueckner-Goldstone-type many-body perturbation theory,[8a] Bethe-Goldstone-type theory,[8b] and CI theory,[8c] only few studies have been performed for molecules.[9] Here we calculate excitation energies, ionization potentials, electron affinities, and spin densities of these molecules. Coupling effects of the spin and electron correlations are also discussed by comparing with the previous result of the PO theory. In the next section

we briefly explain the calculational method, the results are discussed in section 3, and the conclusions of this study are summarized in section 4.

2. CALCULATIONAL METHODS

There are two methods of constructing doublet wavefunctions by the SAC and SAC-CI theories. The first method is to construct the doublet or excited states directly by the SAC theory. The second is to construct the doublet or excited states by the SAC-CI theory using the singlet SAC wavefunction as a reference wavefunction. The former is explained as follows.

First we construct the SAC wavefunction for doublet ground state. Doublet excited states are created by the SAC-CI theory. Namely for doublet ground states, we use the the SAC wavefunction,

$$|\Psi^{SAC}_{g,1/2}\rangle = O_{1/2}\ \exp\Big(\sum_I C_I S^+_I\Big)\,|0\rangle_{1/2}, \qquad (1)$$

where we use the open-shell RHF wavefunction as a reference configuration, and for doublet excited states we use the SAC-CI wavefunction,

$$|\Psi^{SAC\text{-}CI}_{e,1/2}\rangle = \sum_K d_K\big(N_K P R^+_K\big)\,|\Psi^{SAC}_{g,1/2}\rangle = \sum_K d_K \Phi_K, \qquad (2)$$

where $P = 1 - |\Psi^{SAC}_{g,1/2}><\Psi^{SAC}_{g,1/2}|$. In Eq.(1), $|0>_{1/2}$ is a doublet open-shell RHF single determinant. S^+_I is a symmetry-adapted excitation operator in the doublet state and C_I is a variational coefficient. $\sigma_{1/2}$ is a projection operator to doublet space. In Eq.(2) R^+_K is a symmetry adapted excitation operator for the SAC-CI wavefunction. N_K is a normalization factor of Φ_K and d_K is a variational coefficient of the SAC-CI wavefunction. The SAC-CI wavefunction is orthogonal and hamiltonian-orthogonal with the SAC wavefunction of the ground state, as the excited states should be.[2] We call this scheme as method 1 hereafter.

Another method, we call method 2, is as follows. We first calculate singlet SAC wavefunction,

$$|\Psi^{SAC}_{g,0}> = \exp\left(\sum_I C_I S^+_I\right) |0>_0, \qquad (3)$$

where $|0>_0$ is a RHF closed-shell wavefunction. For example, if we want to obtain neutral doublet states, we first calculate cation or anion singlet SAC wavefunction from the cation or anion RHF closed wavefunction $|0>_0$, respectively. Next we calculate doublet SAC-CI wavefunction,

$$|\Psi^{SAC-CI}_{e,1/2}> = \sum_K d_K\left(N_K R^+_K\right) |\Psi^{SAC}_{g,0}>. \qquad (4)$$

In Eq.(4), SAC-CI excitation operator R^+_K is taken as symmetry adapted ionization or electron attachement operator for the singlet anion SAC or singlet cation SAC wavefunction, respectively. Then the wavefunctions of neutral doublet radicals in the ground and excited states are obtained by SAC-CI

theories from Eq.(4).

In the next section, we first compare methods 1 and 2 for the spin and electron correlations in BeH radical. Then for various doublet radicals of chemical interests, we used method 2 since the calculation is more efficient with method 2 than with method 1.

BeH, NH_2, CH_3, and HCO are calculated in the geometries obtained experimentally.[10] For CH_2CH[11b], and CH_3CH_2[12] radicals we used geometry optimized by ab initio calculations. Except for Be, double ζ CGTO which was constructed from Huzinaga's 9s5p basis set[13] to 4s2p based on the contraction scheme of Ellinger et al.[11a,7c]. For the basis set of Be we used Dunning's 3s2p CGTO.[14]

In the calculation of doublet wavefunctions we did not adopt the approximation of frozen core or exclusion of the highest virtual orbitals because spin correlation is described by a balanced cancelation between inner-shell and valence-shell spin-polarizations.[9b] Exclusion of the inner-shell spin-polarization does not cause reasonable result for spin densities.[9c] By the same reason, for the calculation of doublet states, we did not use the configuration selection based on the second-order perturbation energy. Important configurations for the spin correlation are not necessarily important for the electron correlation. Then ordinal configuration selection scheme based on the energy criterion can not take up all of the important spin-polarized configurations.

3. CALCULATED RESULTS AND DISCUSSIONS

3-1. BeH radical by method 1 and method 2.

BeH radical was calculated to compare doublet wavefunctions by method 1 and method 2. Calculated correlation energies are shown in Table 1. Values in the table give the energy lowering from the doublet open-shell RHF wavefunction. The pseudo-orbital (PO) theory gives very small correlation enegy since it consideres only the spin-polarization single excitation within the framework of the SAC theory. Doublet SAC, called method 1, gives -0.02456 a.u. by the variational, SAC-V,[2] and -0.02477 a.u. by the non-variational, SAC-NV,[2] solutions, respectively. These wavefunctions include not only spin correlations but electron correlations. Unlinked effect is as small as -0.0006 or -0.0027 a.u. in comparison with single and double excitation (1+2) CI result since BeH is a smallest doublet system which includes only five electrons. The correlation energies calculated by the doublet SAC-CI, method 2, close to and even lower than the results of method 1. It is noticeable that the rsults of method2, the SAC-CI, is very independent of the choice of the reference configurations, i.e., anion configurations $|BeH^-\rangle$ or cation configurations $|BeH^+\rangle$. From this fact the SAC and SAC-CI theories takes into account not only the spin and electron correlations but also orbital reorganization effects. In Table 2 we give the vertical excitation energy, ionization potential, and electron affinity

of BeH. Both method 1 and 2 give good results for excitation energy. Ionization potential by method 2 is also satisfactory in comparison with the experimental value. The electron affinity is calculated to be -0.418 eV within the basis set of [4s2p/2s] CGTO. Table 3 shows the spin densities obtained by various theories. In this study we partitioned total hfsc in to the RHF contribution and the correlation contribution. The RHF contribution comes from the delocalization of the singly occupied orbital and the correlation contribution comes from the correlation correction to it. BeH is a σ radical and there are large RHF contributions -62.8G and 24.5G for Be and H, respectively. The correlation contributions by the PO theory are 0.7G for Be and 22.7G for H and these come from only the spin correlation effect. Method 1, method 2, and doublet (1+2) CI consider electron correlation as well as spin correlation effects. The effect of electron correlation is 7G 8G for BeH, and as large as 20G 30G for H. The total hfsc of H is much improved by considering electron correlation in comparison with the experimental value.

Thus, we have seen that method 1 and 2 give the similar results for both of the electron and spin correlations, though the unlinked effects are small for BeH. In comparison with the results of the PO theory, there are large coupling effect between spin and electron correlations even for small doublet radical as BeH. It is also noticeable that within method 2 the calculated results are independent of the choice of the reference molecular orbitals, such as orbitals of cation and anion.

3-2. Results of NH_2, CH_3, CH_2CH, CH_3CH_2, and HCO radicals

Next we adopt only the method 2 for calculations of various doublet radicals mainly for the sake of computational efficiency.

NH_2 radical

First we show the result of NH_2 radical. Table 4 gives the correlation energies and Table 5 gives excitation energies, ionization energies, and electron affinities of NH_2. Calculated hfsc's are shown in Table 6. Correlation energies and hfsc's by the SAC-CI theory are also independent of the choice of the reference molecular orbitals as seen in Table 4 and 6. Vertical excitation, ionization energies, and electron affinity are given in Table 5. The result of method 2 is very near to the result of multi-reference double excitation (MRD)-CI by Peyerimhoff et al.[16] Second excitation energy is rather high comparing with the result of MRD-CI where large basis set is used including Rydberg like AO's. For ionization potential, the SAC-CI gives satisfactory result. Calculated hfsc's are listed in Table 6. NH_2 is a π radical and there are only the correlation contribution. Hfsc chaneged from the results of the PO theory by 7G ~ 9G and 5G for N and H, respectively, considering electron correlations. However they are not improved in comparison with the experimental values.

CH_3 radical

We show the correlation energy of CH_3 in Table 7 and ionization potentials and electron affinity in Table 8. The lower excited states of CH_3 radical are assigned to Rydberg excited states.[10] We did not calculate excitation energies since we used only the valence basis set in this study. Calculated hfsc's are shown in Table 9. CH_3 is also π radical. By including electron correlation effects, hfsc of C decreased largely by 11G ~ 17G from the result of the PO theory. On the other hand, the change of hfsc of H was small. zero point vibration effect for the central C of CH_3 was found to be about as large as 10G.[11c,20] Thus the calculated result by the SAC-CI is thought to be reasonable when we consider the vibrational effects included in the experimental value.

In the next paragraphs we show the result of σ radicals such as CH_2CH, CH_3CH_2, and HCO. For these radicals only the method 2 from the anion singlet SAC was used.

CH_2CH radical

Correlation energy and electron affinity of CH_2CH are listed in Table 10 with those of CH_3CH_2 and HCO radicals. These radicals contain two first-row elements and listed values are about twice of those of NH_2 or CH_3 radicals. Hfsc's of CH_2CH, which is a σ radical, is given in Table 11. Total hfsc are partitioned to RHF and correlation contributions. Except for H_α all the hfsc's are improved from the result of the PO theory. For the hfsc at the radical center carbon, the correlation

contribution decreased about 30G from the PO and the total hfsc agreed well with the experimental value. For β-protons hfsc's are also improved by considering the electron correlation by the SAC and SAC-CI theories.

CH_3CH_2 radical

Hfsc s are given in Table 12. Though CH_3CH_2 has a RHF contribution at the radical center carbon, the local electronic structure near the radical center is resemble to that of CH_3, π radical. Then the correlation contribution at the radical center decreases by considering electron correlation effects. Vibrational effect is also seems to be important for the inversion mode as in the case of CH_3 radical. Hfsc of C_α agreed well to the experimental value and those of H_β were also improved from the result of the PO theory. These hfsc's at H_β of CH_2CH and CH_3CH_2 could not be described well by the PO theory in the previous study.[7c]

HCO radical

Finally we give the result of hfsc of HCO radical in Table 13. Hfsc at the carbon, which is a radical center, decreases from the result of the PO theory by 25G and the total constant is fairy good in comparison with the experimental value. Hfsc's of proton is also improved from that of the PO theory.

As seen in the above, large effects of the electron correlations are found in the calculation of spin densities. Except for NH_2 radical the electron correlation effect reduced spin densities at the radical centers and increased those at the α-protons. Symmetry adapted linked and unlinked operators for

electron correlation in the SAC and SAC-CI theories correlates many occupied and virtual orbitals effectively at a time. They delocalize spin densities near the radical centers by the coupling effect with spin correlations. This tendency is obvious especially for σ radicals as seen in the above.

4. CONCLUSIONS

Spin and electron correlations in various doublet radicals are studied by the SAC and SAC-CI theories. For correlation energies, excitation energies, and ionization potentials, satisfactory results are obtained by the SAC and SAC-CI theories, as reported previously for various molecules. For spin densities, the present study has shown the followings; (1) Calculated spin densities by the SAC and SAC-CI theories compare well with the experimental results. (2) The electron correlation couples largely to the spin correlation and calculated spin densities are improved largely from the results of the PO theory. Two methods of constructing the doublet wavefunction are tested in this study; doublet SAC, called method 1, and doublet SAC-CI, called method 2, in the texts. For BeH radical these two method give similar results for both of the spin and electron correlations. Within the method 2, the calculated results are independent from the choice of the molecular orbitals in the reference wavefunction, such as anion or cation orbitals. This is a result that the SAC and SAC-CI

theories include not only the spin and electron correlations but also orbital reorganization effect correctly.

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REFERENCES

1. H.Nakatsuji and K.Hirao, J.Chem.Phys. 68, 2053 (1978).

2. H.Nakatsuji, Chem.Phys.Lett. 59, 362 (1978); H.Nakatsuji, Chem.Phys.Lett. 67, 329 (1979).

3. H.Nakatsuji, Chem.Phys.Lett. 67, 334 (1979).

4. H.Nakatsuji and K.Hirao, Int.J.Quantum.Chem. 20, 1301 (1981); K.Hirao and H.Nakatsuji, Chem.Phys.Lett. 79, 292 (1981); H.Nakatsuji, K.Ohta, and K.Hirao, J.Chem.Phys. 75, 2952 (1981).

5. H.Nakatsuji and T.Yonezawa, Chem.Phys.Lett., in press.

6. L.S.Cederbaum, Mol.Phys. 28, 479 (1974); U.Gelius, J.Electroc Spectrosc. 5, 985 (1974).

7. (a) H.Nakatsuji and K.Hirao, Chem.Phys.Lett. 47, 569 (1977); (b) H.Nakatsuji and K.Hirao, J.Chem.Phys. 68, 4279 (1978); (c) K.Ohta, H.Nakatsuji, K.Hirao, and T.Yonezawa, J.Chem.Phys. 73, 1770 (1980).

8. (a) H.P.Kelly, Phys.Rev. 173, 142 (1968); H.P.Kelly and A.Ron, Phys.Rev. A2, 1261 (1970); E.S.Chang, R.T.Pu, and T.P.Das, Phys.Rev. 174, 1 (1968); N.C.Dutta, C.Matsubara, R.T.Pu, and T.P.Das, Phys.Rev.Lett. 21, 1139 (1968); Phys.Rev. 177, 33 (1969); J.D.Lyons, R.T.Pu, and T.P.Das, Phys.Rev. 178, 103 (1969); 186, 266 (1969); T.Lee, N.C.Dutta, and T.P.Das, Phys.Rev. A1, 995 (1970); J.Hata, J.Chem.Phys. 62, 1221 (1975); (b) R.K.Nesbet, Colloq.Int.Center Natl.Rech.Sci. (Paris) 164, 87 (1967); Phys.Rev. A2, 661 (1970); Phys.Rev. A4, 1208 (1970); (c) O.R.Platas and H.F.Schaefer, Phys.Rev. A4, 33 (1971).

9. (a) C.F.Bender and E.R.Davidson, Phys.Rev. 183, 292 (1969); (b) S.Y.Chang, E.R.Davidson, and G.Vincow, J.Chem.Phys. 52, 1740 (1970); (c) C.F.Jackels and E.R.Davidson, J.Chem.Phys. 63, 4672 (1975); (d) J.E.Rodgers, T.Lee, T.P.das, and D.Ikenberry, Phys.Rev. A7, 51 (1973); J.E.Rodgers and T.P.Das, Phys.Rev. A8, 2195 (1973).

10. G.Herzberg, Electronic Spectra of Polyatomic Molecules (Van Nostrand, Princeton, 1967); K.P.Huber and G.Herzberg, Molecular Spectra and Molecular Structure (Van Nostrand, NY, 1979).

11. (a) Y.Ellinger, A.Rassat, R.Subra, and G.Berthier, J.Chem.Phys. 62, 1 (1975); Y.Ellinger, R.Subra, B.Levy, P.Millie, and G.Berthier, J.Chem.Phys. 62, 10 (1975); (b) P.Millie and G.Berthier, Int.J.Quantum.Chem. s2, 67 (1968); P.Millie, B.Levy, and G.Berthier, Int.J.Quantum. Chem. 6, 155 (1972); (c) V.Barone, J.Douady, Y.Ellinger, R.Subra, and F.Pauzat, Chem.Phys.Lett. 65, 542 (1979); Y.Ellinger, F.Pauzat, V.Barone, J.Douady, and R.Subra, J.Chem.Phys. 72, 6390 (1980).

12. J.Pacansky and M.Dupuis, J.Chem.Phys. 68, 4276 (1978).

13. S.Huzinaga, J.Chem.Phys. 42, 1293 (1965).

14. T.H.Dunning, Jr.and P.J.Hay, in Modern Theoretical Chemistry , edited by H.F.Schaefer III (Plenum, NY, 1977), Vol.3, p.1.

15. L.B.Knight, Jr., J.M.Brom, Jr., and W.Weltner, Jr., J.Chem.Phys. 56, 1152 (1972).

16. S.D.Peyerimhoff and R.J.Buenker, Can.J.Chem. 57, 3182 (1979).

17. S.J.Dunlavey, J.M.Dyke, N.Jonathan, and A.Morris, Mol.Phys. 39, 1121 (1980).

18. S.Forner, E.L.Cochran, V.A.Bowers, and C.Jen, Phys.Rev.Lett. 1, 91 (1958).

19. R.W.Fessenden, J.Phys.Chem. 71, 74 (1967); R.W.Fessenden and R.H.Schuler, J.Chem.Phys. 39, 2147 (1963).

20. D.L.Beveridge and K.Miller, Mol.Phys. 14, 401 (1968); B.T.Sutcliffe and C.Gaze, Mol.Phys. 35, 525 (1978).

21. R.W.Holmberg, J.Chem.Phys. 51, 3255 (1969).

Table 1. Correlation energy of BeH ($^2\Sigma^+$) in a.u.

Method	Reference config.	Ecorr. (a.u)
open-shell RHF	------	-15.14361
Pseudo-Orbital	|BeH>	-0.00070
(1+2)CI	|BeH>	-0.02450
Method 1. (Doublet SAC)		
SAC-V	|BeH>	-0.02456
SAC-NV	|BeH>	-0.02477
Method 2. (SAC-CI from singlet SAC)		
SAC-CI-V	|BeH^->	-0.02493
SAC-CI-NV	|BeH^->	-0.02283
SAC-CI-V	|BeH^+>	-0.02485

Table 2. Excitation, ionization energies and electron affinity of BeH radical (eV).

Excitation energy	$^2\Sigma^+ - {}^2\Pi$
Method 1.	2.76
Method 2.	2.60
Exptl.[a]	2.48
Ionization potential	
Method 2.	8.19
Exptl.[a]	8.21
Electron affinity	
Method 2.	-0.418

a: Ref.10

Table 3. Hyperfine splitting constants of BeH ($^2\Sigma^+$) in gauss unit.

Method	Reference config.	hfsc Be SD	Be SP	Be Total	H SD	H SP	H Total
open-shell RHF		-62.8	0.0	-62.8	24.5	0.0	24.5
Pseudo-Orbital	|BeH>	-62.8	0.7	-62.1	24.5	22.7	47.2
(1+2)CI	|BeH>	-62.8	7.6	-55.2	24.5	48.7	73.2
Method 1.							
SAC	|BeH>	-62.8	7.9	-54.9	24.5	52.6	77.1
Method 2.							
SAC-CI-V	$\|BeH^->$	-62.8	7.7	-55.1	24.5	42.7	67.2
SAC-CI-NV	$\|BeH^->$	-62.8	6.9	-55.9	24.5	42.1	66.6
SAC-CI-V	$\|BeH^+>$	-62.8	6.6	-56.2	24.5	42.1	66.6
Exptl.[a]				-74.1			69.1

SD: Results of open-shell RHF wavefunction.
SP: Spin-polarization effects by correlated wavefunctions.
a: Ref.15

Table 4. Correlation energy of NH_2 ($^2B_1$)

Method	Reference config.	Ecorr. (a.u.)
open-shell RHF		-55.5265
Method 2.		
SAC-CI-V	$\|NH_2^->$	-0.1080
SAC-CI-NV	$\|NH_2^->$	-0.1020
SAC-CI-V	$\|NH_2^+>$	-0.1076
SAC-CI-NV	$\|NH_2^+>$	-0.1010

Table 5. Excitation, ionization energies and electron affinity of NH_2 radical (eV).

Excitation energy	$^2B_1 \longrightarrow {}^2A_1$	$^2B_1 \longrightarrow {}^2B_2$
SAC-CI-V	2.13	7.47
SAC-CI-NV	2.12	7.46
MRD-CI[a]	2.16	6.64
Ionization potential		
SAC-CI-V	12.6	
SAC-CI-NV	12.4	
Exptl.[b]	12.5	
Electron affinity		
SAC-CI-V	-2.38	
SAC-CI-NV	-2.21	

a: S. D. Peyerimhoff et.al. Ref.16
b: Ref.17

Table 6. Hyperfine splitting constants of NH_2 ($^2B_1$) in gauss unit.

Method	Reference config.	hfsc N	hfsc H
open-shell RHF		0.0	0.0
Pseudo-Orbital	$\|NH_2>$	7.4	-24.2
Method 2.			
SAC-CI-V	$\|NH_2^->$	14.3	-18.8
SAC-CI-NV	$\|NH_2^->$	15.7	-19.3
SAC-CI-V	$\|NH_2^+>$	16.2	-18.7
SAC-CI-NV	$\|NH_2^+>$	16.6	-19.4
Exptl.[a]		10.3	-23.9

[a]: Ref.18

Table 7. Correlation energy of CH_3 ($^2A''$).

Method	Reference config.	Ecorr. (a.u.)
open-shell RHF		-39.5373
Method 2.		
SAC-CI-V	$\|CH_3->$	-0.1065
SAC-CI-NV	$\|CH_3->$	-0.1006
SAC-CI-V	$\|CH_3^+>$	-0.1066
SAC-CI-NV	$\|CH_3^+>$	-0.1025

Table 8. Ionization potential and electron affinity of CH_3 (eV).

	SAC-CI-V	SAC-CI-NV	Exptl.[a]
Ip	10.29	10.17	9.84
Af	-2.76	-2.59	----

[a]: Ref.10

Table 9. Hyperfine splitting constants of CH_3 ($^2A''$) in gauss unit.

Method	Reference config.	hfsc	
		C	H
open-shell RHF		0.0	0.0
Pseudo-Orbital	$\|CH_3>$	39.4	-26.5
Method 2.			
SAC-CI-V	$\|CH_3->$	26.8	-21.0
SAC-CI-NV	$\|CH_3->$	28.4	-21.9
SAC-CI-V	$\|CH_3+>$	22.4	-21.3
SAC-CI-NV	$\|CH_3+>$	24.8	-22.3
Exptl.[a]		38.3	-23.0

a: Ref.19

Table 10. Correlation energy and electron affinity[a] of CH_2CH ($^2A''$), CH_3CH_2 ($^2A''$), and HCO ($^2A''$) radicals.

Correlation energy (a.u.)

Radical	RHF-open	SAC-CI-V	SAC-CI-NV
CH_2CH	-77.3438	-0.1822	-0.1817
CH_3CH_2	-78.5499	-0.1854	-0.1851
HCO	-113.1779	-0.2383	-0.2116

Electron affinity (eV)

Radical	SAC-CI-V	SAC-CI-NV
CH_2CH	-1.41	-1.40
CH_3CH_2	-2.52	-2.51
HCO	-2.48	-1.66

a: Results from singlet anion SAC wavefunction.

Table 11. Hyperfine splitting constants of CH_2CH ($^2A''$) in gauss unit.

		PO	SAC-CI-V	SAC-CI-NV	Exptl.[a]
C	SD	119.4	119.4	119.4	
	SP	23.0	-4.5	-6.0	
	Total	142.4	114.9	113.4	107.6
C_α	SD	9.5	9.5	9.5	
	SP	-23.2	-16.2	-16.9	
	Total	-13.7	-6.7	-7.4	-8.6
H_α	SD	23.5	23.5	23.5	
	SP	-12.4	-6.1	-6.1	
	Total	11.1	17.4	17.4	13.3
H_β^{cis}	SD	12.9	12.9	12.9	
	SP	11.5	16.2	16.4	
	Total	24.4	29.1	29.3	34.2
H_β^{trans}	SD	21.8	21.8	21.8	
	SP	17.5	25.7	25.7	
	Total	39.3	47.5	47.5	68.5

a: Ref.19

Table 12. Hyperfine splitting constants of CH_3CH_2 ($^2A''$) in gauss unit.

		PO	SAC-CI-V	SAC-CI-NV	Exptl.[a]
C	SD	2.54	2.54	2.54	
	SP	42.61	21.05	21.39	
	Total	45.15	23.59	23.93	39.07
H_α	SD	0.21	0.21	0.21	
	SP	-26.22	-18.43	-18.88	
	Total	-26.01	-18.22	-18.67	-22.39
C_α	SD	0.11	0.11	0.11	
	SP	-18.34	-13.11	-13.75	
	Total	-18.23	-13.00	-13.64	-13.57
H_β	SD	11.24	11.24	11.24	
	SP	9.33	11.17	11.48	
	Total	20.57	22.41	22.72	26.87

a: Ref.19

Table 13. Hyperfine splitting constants of HCO ($^2A''$) in gauss unit.

		PO	SAC-CI-V	SAC-CI-NV	Exptl.[a]
C	SD	154.8	154.8	154.8	
	SP	4.4	-20.6	-20.5	
	Total	159.1	134.2	134.3	131.0
O	SD	-3.9	-3.9	-3.9	
	SP	-10.2	-4.9	-5.4	
	Total	-14.1	-8.8	-9.3	---
H	SD	84.7	84.7	84.7	
	SP	24.5	29.7	30.6	
	Total	109.2	114.4	115.3	127.0

a: Ref.21

PART II, Chapter 3

Spin and Electron Correlations in Various Excited States of NO_2 and NO_2^+

I. INTRODUCTION

The nitrogen dioxide is a stable free radical and it has long been the object of many experimental and theoretical studies. In the previous theoretical works, electron correlation effect was shown to be very important to the ground and various excited states of NO_2 radical by large scale CI, MCSCF-CI, and muliti-reference CI (MR-CI) approaches[1-5]. CI wavefunction, however, requires many electronic configurations because of its linearity of expansion. Moreover the wavefunction of the excited states, should satisfy the orthogonality and the hamiltonian-orthogonality with the ground state wavefunction. The MCSCF-CI or the MR-CI theories, however, do not satisfy these necessary conditions for excited states when their orbital bases are optimized for each of the ground and excited states. These non-orthogonalities are not favorable from the theoretical point of view. Here we study the ground and excited states of NO_2 and NO_2^+ by symmetry-adapted-cluster (SAC) and SAC-CI theories[6]. The SAC expansion is based on the cluster expansion theory and converges faster than the CI expansion by its non-linearity. For excited states, the SAC-CI wavefunction is constructed from the SAC wavefunction and it reorganizes the correlation effect introduced by the SAC wavefunction. It is orthogonal and orthogonal with respect to the hamiltonian with the SAC wavefunction of the ground state and suited for various excited states. These theories have already given good results for the ground and various excited states of H_2O, H_2CO, and CH_2 molecules including their ionized and electron attached states[7].

Furthermore, these theories have given fairly good results for the spin correlation in various doublet radicals and the coupling of spin and electron correlation has shown to be very important[8].

In this section, we study systematically the excitation energies, ionization potentials, and spin densities of NO_2 radical by the SAC and SAC-CI theories. There are few studies on the spin density of NO_2 radical with correlated wavefunctions[1]. The spin densities by the open-shell orbital theoretic approaches are compared with the result of the SAC and SAC-CI theories.

In the next section we describe the computational detailes. Results and discussions are given in the Sec.III and Sec.IV for excitation energies and spin densities, respectively. Conculsion is given in Sec.V.

II. METHOD OF CALCULATION.

In this study we first calculated the SAC wavefunction of NO_2^+ in the ground state. Then the excited states of NO_2^+ and the ground and excited states of NO_2 radical were calculated by the SAC-CI theories. The basis set used here is Dunning's [4s2p] CGTO[9] augmented by the nitrogen-centered diffuse functions (three of s-type exponents 0.07, 0.02, and 0.006 and two full-component p gaussians with exponents 0.05 and 0.015 respectively)[5]. The molecular geometry was fixed to the experimental geometry[10] of the ground state of NO_2 radical.

r(NO) is 1.1934Å and ∠ONO is 134.1° in C_{2v} geometry. The molecule oriented such that the z axis is parallel to the C_2 axis and z points from the O-O midpoint toward N. The y axis is parallel to the O-O line and x points out of the molecular plane. The reference Hartree Fock wavefunction for the SAC and SAC-CI calculation was obtained by the Roothaan's SCF method for NO_2^+. In the previous work[8], it has been proved that the calculated results of valence excitations and spin densities do not depend on the selection of molecular orbitals in the reference configuration and that the SAC and SAC-CI theories include enough the orbital reorganization effect. The SCF equation was solved for the $^1A_1$ state of NO_2^+. The configuration is,

$$...(5a_1)^2(1b_1)^2(3b_2)^2(1a_2)^2(4b_2)^2(6a_1)^0(2b_1)^0....$$

We use these molecular orbitals systematically in all of the SAC and SAC-CI calculations of the states of NO_2 and NO_2^+. Frozen core approximation or elimination of the highest virtual orbitals was not used for NO_2 since the spin correlation is determined by the cancellation between the inner-shell and the valence-shell spin polarization effects[12]. For the calculation of spin density we did not use configuration selection and all of the linked excitation operators are considered in the doublet ground state of NO_2. Spin polarized excited configurations are necessary to describe the spin correlation correctly. From the energetical point of view, however, they correspond to rather high energy configurations and not so important for the electron correlation of the doublet ground state. If the configuration selection is performed, these configurations will be deleted out

from the wavefunction of the ground state. For the calculation of excitation energies of NO_2 and NO_2^+, however, configuration selection was performed for the SAC and SAC-CI calculations.

III. VERTICAL EXCITATION SPECTRA OF NO_2 and NO_2^+

A. NO_2

Calculated total energy by the SAC-CI theory was -204.300185 a.u. and the correlation energy was amounted to -0.340718 a.u. relative to -203.959468 a.u. of the open-shell RHF theory. The vertical excitation energies are given in Table I along with the corresponding experimental and theoretical values. Column 1 gives the state label and column 2 the excitation picture from the X^2A_1 ground state HF configuration. Column 3 and 4 give the results of SAC-CI(V), which was solved variationally[7c], and SAC-CI(NV), which was solved non-variationally[7c], and column 5 gives some experimental results available. Column 6-8 are the results of some other theoretical works[3,5]. The calculated values by the SAC-CI wavefunction are in good agreement with the experimental results for both of the valence and Rydberg excitations. The results of the single-reference CI (SR-CI) or MR-CI[5] is slightly better than the present result; the numbers of configurations used in these CI are about ten times as large as that of the present SAC-CI calculations. The SR-CI or MR-CI wavefunctions are not orthogonal and othogonal with respect to the hamiltonian with one another and the wavefunctions of the excited states contain

the component of the ground state or other excited states of the same symmetry. In the study of Benioff[3], it was found that the d-polarization functions lowers the ground state energy mainly. Then, the excitation energies become larger in comparison with the calculation without d-function. Thus, if we consider the effect of d-polaization functions in the present calculation, the excitation energies will be improved. For the excitation from $6a_1$ to 3p Rydberg states, the order of near degenerate three states, $^2B_1$, $^2A_1$, and $^2B_2$, obtained by the SAC-CI are different from the order by the MR-CI. The data of MR-CI, however, are not the results of the direct calculation of these states but the estimated values assuming that the additional energy lowering by the MR-CI relative to the SR-CI is the same as those explicitly calculated for the corresponding ($^1A_1$) state of the cation in Table II.

B. NO_2^+

Table II presents the vertical ionization potentials of NO_2 radical. The wavefunction of the $^1A_1$ state is obtained by the SAC wavefunction. The agreement between the calculated values and the experimental values is good. In the first two states, however, the agreement with the experiments is not so good. The SAC-CI gives better ionization potentials than the CI except for the first two states. We also showed the singlet-triplet separation for three excited states in Table III. The separation, except for B_1 states, are in good agreement with the experimental value. The value of separation

is calculated to be largest for B_2 state in these three states. This is understood qualitatively as follows. The singlet-triplet splitting is thought to be approximately proportional to the value of exchange integral between the ionized orbital and the singly occupied orbital which is the $6a_1$ σ non-bonding orbital NO_2 radical in the ground state. The ionized orbital in B_1 state is $1b_1$, π bonding and that of the A_2 state is $1a_2$, π anti-bonding orbital. On other hand, the ionized orbital in the B_2 state is is $4b_2$ which is σ NO bonding orbital and the exchange integral thought to be larger than those in B_1 and A_2 states.

IV. SPIN DENSITY OF NO_2 RADICAL

The frozen core approximation, the elimination of the highest virtual orbitals, and configuration selections are not adequet in the calculation of spin density, as mentioned previously. Then, the number of the SAC-CI linked operator was amounted to 2644 in the ground state, $^2A_1$. In Table IV, we showed the calculated spin density as the ESR isotropic hyperfine splitting constant (hfsc) in unit of gauss. NO_2 is a doublet σ radical and the unpaired electron is located at the N non-bonding orbital in the HF configuration. The results of the orbital theoretic approaches, UHF[13a,b], anihilated UHF[13c] (AUHF) and pseudo-orbital (PO)[14] theories are also given in Table IV with the same basis set and geometry as in the SAC-CI calculation. The UHF wavefunction is not spin adapted and its

self-consistency effect is not adequet for the spin-correlation problem[15]. The calculated results are too large for N. The AUHF gives very poor result as well as the UHF theory since the inadequet self-consistency effect of the UHF theory can not be cured only by the spin anihilation or the spin projection[6a,1]. The difference between the UHF and the AUHF result is large at the oxygen hfsc and very small for nitrogen. This is understood qualitatively that the spin contaminations in the UHF wavefunction mainly come from the diradical nature at the two oxygens. The PO theory consideres only one-electron ecitations in the SAC theory and here it considers only the spin-polarization effect. Then the PO theory is essentially within the orbital theoretic approach. It gives a good result for both of nitrogen and oxygen hfs constants. The results of the SAC-CI, which considers the spin and electron correlation effects at the same time, gives good results for the oxygen hfsc as well as the PO theory. For nitrogen, however, the spin density was reduced largely from the values of the PO theory by the coupling effect of the electron and spin correlations. This may come from the inadequacy of the basis set used here. The contraction of the basis set used here is deferent from the previous scheme[14c] suited for the calculation of spin densities. The decreasing of the spin density at the radical center by considering the electron correlation, however, has been found in the previous study for many doublet radicals by SAC and SAC-CI theories[8]. The result of CI by Jackels et al. gives good result for the hfsc of N though they used 3-frozen core approximation[1].

V. CONCLUSION

The vertical excitation energies, ionization potentials, and hfs constants of NO_2 were studied by the SAC and SAC-CI theories. All of the calculated results were obtained by using the same molecular orbital for NO_2^+ in the reference configuration of the SAC and SAC-CI theories. This simple treatment allows us to analyze the calculated results systematically. Calculated excitation energies of NO_2 were fairly good in comparison with the experimental values. d-polarization functions, however, is known to raise the excitation energy and they should be included for a more improved values of excitation energies[2,3]. The agreement of the calculated ionization potential with the experimental values was good and singlet triplet separation was also studied by the SAC and SAC-CI theories. For hfs constants of NO_2 radical, the result of UHF and AUHF were very poor. The PO theory gave best result for hfsc of NO_2. The electron correlation effect for hfsc was large though it reduced the spin density largely at the radical center, N. This may come from the inadequacy of the basis set used here. This is the same tendency in the previous study[8] of doublet radicals by the SAC and SAC-CI theories.

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REFERENCES

1. C.F.Jackels and E.R.Davidson, J.Chem.Phys. 63, 4672 (1975).

2. N.C.Handy, J.D.Goddard, and H.F.Schaefer III, J.Chem.Phys. 71, 426 (1979).

3. P.Benioff J.Chem.Phys. 68, 3405 (1978).

4. G.D.Gillispie, A.U.Khan, A.C.Wahl, R.P.Hosteny, J.Chem.Phys. 63,3425 (1975); G.D.Gillispie and A.U.Khan, J.Chem.Phys. 65, 1624 (1976).

5. S.K.Shih, S.D.Peyerimhoff, and R.J.Buenker, Chem.Phys.Lett. 46, 201 (1977).

6. (a) H.Nakatsuji and K.Hirao, J.Chem.Phys. 68, 2053, 4279 (1978). (b) H.Nakatsuji, Chem.Phys.Lett. 59, 362 (1978). (c) H.Nakatsuji, Chem.Phys.Lett. 67, 329, 334 (1979).

7. (a) H.Nakatsuji and K.Hirao, Int.J.Quantum.Chem. 20, 1301 (1981). (b) K.Hirao and H.Nakatsuji Chem.Phys.Lett. 79, 292 (1981). (c) H.Nakatsuji, K.Ohta, and K.Hirao, J.Chem.Phys. 75, 2952 (1981). (d) H.Nakatsuji and T.Yonezawa, Chem.Phys.Lett., in press.

8. H.Nakatsuji, K.Ohta, and T.Yonezawa, to be published.

9. T.H.Dunning, J.Chem.Phys. 53, 2823 (1970).

10. G.Herzberg, Electronic Spectra of Polyatomic Molecules (Van Nostrand, Princeton, 1967).

11. C.C.J.Roothaan, Rev.Mod.Phys. 23, 69 (1951).

12. S.Y.Chang, E.R.Davidson, and G.Vincow, J.Chem.Phys. 52, 1740 (1970).

13. (a) J.A.Pople and R.K.Nesbet, J.Chem.Phys. 22, 571 (1954). (b) A.T.Amos and G.G.Hall, Proc.R.Soc. A263, 483 (1961). (c) A.T.Amos and L.C.Snyder, J.Chem.Phys. 41, 1773 (1964).

14. (a) H.Nakatsuji and K.Hirao. Chem.Phys.Lett. 47, 569 (1977). (b) H.Nakatsuji and K.Hirao, J.Chem.Phys. 68, 4279 (1978). (c) K.Ohta, H.Nakatsuji, K.Hirao, and T.Yonezawa, J.Chem.Phys. 73, 1770 (1980).

15. (a) H.Nakatsuji, H.Kato, and T.Yonezawa, J.Chem.Phys. 51, 3175 (1969). (b) H.Nakatsuji, J.Chem.Phys. 59, 2586 (1973). (1970).

Table I. Vertical excitation energies of NO (eV).

State	Excitation	SAC-CI-V	SAC-CI-NV	Exptl.[a]	SRCI[a]	MRCI[a]	MCSCF-CI[b]	
							[4s3p]	[4s3p1d]
$^2B_1$	$6a_1 - 2b_1$	2.70		2.81-2.84		2.79	2.60	2.93
$^2B_2$	$4b_2 - 6a_1$			3.10		3.22	3.36	3.40
$^2A_2$	$1a_2 - 6a_1$					3.25	3.54	3.61
$^2A_1$	$6a_1 - 3s$	7.11	7.12	7.5	7.96	7.71[c]		
$^2B_1$	$6a_1 - 3px$	8.05	8.06		9.09	8.84[c]		
$^2A_1$	$6a_1 - 3pz$	8.06		8.6	8.98	8.73[c]		
$^2B_2$	$6a_1 - 3py$	8.29			8.87	8.87[c]		

a: Results of single-reference (SR) CI and multi-reference (MR) CI of Reference 5.

b: Reference 3

c: Result was estimated by assuming that the MRCI lowering for this Rydberg state relative to SRCI treatment is the same as that explicitly calculated for the corresponding ($^1A_1$) state of NO_2^+ in Table II. See also reference 5.

Table II. Vertical ionization potentials of NO_2 (eV).

State	Ionization	SAC-CI-V	SAC-CI-NV	Exptl.[a]	SRCI[a]	MRCI[a]
$^1A_1$	$6a_1 - \infty$	10.66	10.59	11.25	11.39	11.14
$^3B_2$	$4b_2 - \infty$	12.69	12.69	13.02	12.82	
$^3A_2$	$1a_2 - \infty$	13.42	13.41	13.60	13.25	
$^1A_2$	$1a_2 - \infty$	13.96	13.93	14.07	13.55	
$^1B_2$	$4b_2 - \infty$	14.59	14.58	14.97	14.38	14.38
$^3A_1$	$5a_1 - \infty$	18.04	18.03			
$^3B_1$	$1b_1 - \infty$	18.97	18.95			
$^1B_1$	$1b_1 - \infty$	19.75	19.73			

a: Reference 5

Table III. Singlet triplet separation in excited states of NO_2^+ (eV).

State	Ionization	SAC-CI-V	SAC-CI-NV	Exptl.[a]	SRCI[a]
B_2	$4b_2 - \infty$	1.90	1.89	1.81	1.81
A_2	$1a_2 - \infty$	0.53	0.53	0.32	0.30
B_1	$1b_1 - \infty$	0.79	0.78	0.34	

a: Reference 5

Table IV. Spin densities[a] of NO_2 ($^2A_1$) (gauss).

Method	N	O
UHF[b]	74.7(74.9)	-14.5(-8.95)
AUHF[c]	74.8(74.9)	-10.8(-8.95)
PO	45.3(43.6)	-14.7(-8.40)
SAC-CI-V	37.7	-13.5
SAC-CI-NV	36.4	-14.5
CI[d]	59.7	-22.6
Exptl.	54.8	-16.3

a: In the parentheses, spin delocalization contributions are given.

b: $S(S+1) = 0.7688$

c: $S(S+1) = 0.7511$

d: (1+2)CI. Reference 1.

CHAPTER 4

SUMMARY

In Part II, the spin and electron correlations of various doublet radicals have been studied by the SAC and SAC-CI theories. Calculated results have been compared with experimental values and previous theoretical results of some orbital theories. Coupling effect of spin and electron correlations has been found large. In chapter 2, for energetic properties of various radicals, such as excitation and ionization energies, the SAC and SAC-CI theories have given satisfactory result in comparison with experimental values. The calculated spin densities are affected largely from the electron correlations introduced by the SAC and SAC-CI theories and various important spin distributions have been improved in comparison with the PO theory which considers only the spin correlation effect. Moreover, the result of the SAC and SAC-CI theories was independent from the choice of molecular orbitals in the reference configuration and orbital reorganization effect is also included enough in these theories. In chapter 3, vertical excitation energies, ionization potentials, and spin densities of NO_2 radical have been investigated. The correlation effect of NO_2 radical is very large and the orbital theory does not give a reasonable result for the electronic and spin structures. The SAC and SAC-CI wavefunctions have given good result for energetic properties in ground state, excited states, and ionized states. The calculated spin density of the PO theory was apparently better than the results of the SAC and SAC-CI theories. The coupling effect of spin and electron

correlations, however, was very large especially near the radical center. The UHF and anihilated UHF (AUHF) theories did not give reasonable results for spin densities because of the incorrect spin symmetry or self-consistency effects thereof.

PART III

ELECTRON CORRELATIONS IN GROUND AND VARIOUS EXCITED STATES STUDIED BY THE SAC AND SAC-CI THEORIES

CHAPTER 1

INTRODUCTION

In this part, the electron correlation problem in ground state, valence and Rydberg excited states, ionized states, and electron attached states of molecules of chemical interests have been studied by the SAC and SAC-CI theories. In chapter 2 we applied these theories to formaldehyde. The valence and Rydberg excited states of formaldehyde have been investigated extensively by experimental and theoretical methods. The experimental aspects of the excited states were reviwed by Moule and Walsh[1] and the mixing of valence and Rydberg excitations are of interests[2-4]. The nature of electron attached states[5], however, still seems uncertain. Here we calculate the ground state by the SAC theory. Singlet and triplet excited states, ionized states, and electron attached states are calculated by the SAC-CI theory. As excited states we study both valence and Rydberg states, and mixing thereof especially for the singlet $\pi - \pi^*$ state. In chapter 3, Rydberg excited states and ionized states of NH_2 and CH_3 radicals are studied. Though these are the most basic free radicals, there are few experimental and theoretical studies for their Rydberg states[6]. Singlet and triplet excited states of NH_2^+ and CH_3^+ are also calculated by the SAC-CI wavefunction and obtained ionization potentials are compared with the experimental values.

References

1. D.C.Moule and A.D.Walsh, Chem.Rev. 75, 292 (1981).

2. D.L.Yeager and V.McKoy, J.Chem.Phys. 60, 2714 (1974).

3. S.R.Langhoff and E.R.Davidson, J.Chem.Phys. 64, 4699 (1976).

4. L.B.Harding and W.A.Goddard III, J.Am.Chem.Soc. 97, 6293 (1975); 99, 677 (1977).

5. E.H. Van Veen, W.L. Van Dijk, and H.H. Brongersma, Chem.Phys. 16, 337 (1976); P.D.Burrow and J.A.Michejda, Chem.Phys.Lett. 42, 223 (1976).

6. S.D.Peyerimhoff and R.J.Buenker, Can.J.Chem. 57, 3182 (1979); G.T.Surratt and W.A.Goddard III, Chem.Phys. 23, 39 (1977); R.McDiarmid, Theoret.Chim.Acta(Berl.) 20, 282 (1971); Y.Ishikawa and R.C.Binning Jr., Chem.Phys.Lett. 40, 342 (1976).

PART III, Chapter 2

Ground State, Valence and Rydberg Excited States, Ionized States, and Electron attached States of Formaldehyde

I. INTRODUCTION

In this series of studies we are developing cluster expansion theories not only for closed shell ground states but also for open shell and excited states, ionized states, and electron attached states.[1-6] The SAC (symmetry-adapted-cluster) theory was developed for closed and open shell ground states[1] and recently extended to excited states.[6] SAC-CI theory was developed for excited states, ionized states, and electron attached states.[3,4] It utilizes the fact that the subspace of the SAC ground state spans an adequate basis for excited states, ionized states, and electron attached states. Physically, this means that the electron correlation in the ground state gives a good starting point for the study of electron correlations in these excited states. In the cluster expansion formalism, Paldus *et al.*,[7] Lindgren,[8] and Ohmine[9] have also given interesting approaches to open shell and excited states.

We have given the theories for the SAC and SAC-CI expansions in previous papers.[1,3] Formulations for actual applications (programming) of the theories were summarized in two previous papers.[4,5] Applications were given for some simple systems (Be, BH_3, and H_2O) with the first version of the program.[4] The results were excellent in comparison with the full or nearly full CI results for both ground and singlet excited states. More systematic applications to H_2O for the ground state, singlet and triplet excited states, ionized states, and electron attached states were given previously with the use of the second version of the program.[5] The results showed satisfactory agreements with experiments. Applications of the SAC theory to excited states were reported for Be, H_2O, and CH_2 with excellent agreement with experiment.[6] For excited states, the SAC-CI theory is easier and less time consuming than the SAC theory, though the latter will give more accurate results.

In this paper, we apply the SAC and SAC-CI theories to formaldehyde. Formaldehyde is a molecule for which spectroscopic studies are widely reported from both experimental[10-14] and theoretical[15-25] works. The experimental aspects of the excited states were reviewed in detail by Moule and Walsh.[10] The valence and Rydberg excitations and the mixing thereof are of interest.[15-22] The photoelectron spectra are well studied[12,13] and different assignments were made by different theories.[24] The nature of the electron attached states[11,14] still seems uncertain. Formaldehyde thus includes chemical complexities well and yet is very small, so that it is a good subject for testing of new theories. We calculate here the ground state by the SAC theory.[1] Singlet and triplet excited states, ionized states, and electron attached states are calculated by the SAC-CI theory.[3] As excited states we study both valence and Rydberg states, and a mixing thereof (especially for the singlet $\pi - \pi^*$ state). The computational scheme used here is the same as the one used previously for H_2O.[5]

II. CALCULATIONAL DETAILS

A. Basis sets and geometry

Two kinds of basis sets were used in order to study mixing between valence and Rydberg excited states. One is the double zeta [3*s*2*p*/2*s*] CGTO's of Huzinaga[26] and Dunning[27] (valence only basis). The other includes a valence basis plus Rydberg basis (single GTO's with exponents 0.023 and 0.021 for 3*s* and 3*p* AO's, respectively, of carbon and 0.032 and 0.028 for 3*s* and 3*p* AO's, respectively, of oxygen).[27] This basis is denoted the valence and Rydberg basis. The experimental geometry[28] $R_{CO} = 1.2099$ Å, $R_{CH} = 1.1199$ Å, and $\angle HCH = 118°$ was used for all calculations. The molecule lies on the *yz* plane with the *z* axis parallel to the CO bond.

B. Calculational method

The ground state was calculated by the SAC expansion around the Hartree-Fock reference state $|0\rangle$:

$$\Psi_t = \exp\left(\sum_I C_I S_I^\dagger\right)|0\rangle \ , \tag{1}$$

where $S_I^\dagger$ is a symmetry-adapted (singlet c_1) excitation operator. The expansion was terminated at second order in the coefficients

$$\Psi_\ell \simeq \left[1 + \sum_I C_I S_I^\dagger + \left(\frac{1}{2}\right) \sum_{IJ} C_I C_J S_I^\dagger S_J^\dagger\right] |0\rangle \ . \qquad (2)$$

As linked configurations $S_I^\dagger|0\rangle$, we have included all single and double excitations from the reference $|0\rangle$. In the unlinked configurations $S_I^\dagger S_J^\dagger|0\rangle$, we have included quadruple excitations as products of double excitations. It takes account of the "simultaneous collisions" of electrons in different spaces of molecules.[29] For the closed shell ground state, double and triple excitations in the unlinked terms can be neglected.[29,30] For practical reasons, the double excitations included in the unlinked terms $S_I^\dagger S_J^\dagger|0\rangle$ were those which have coefficients larger than 10^{-3} in the CI expansion including all single and double excitations. Of the two methods of solving the SAC equation (variational and nonvariational),[3] we have used only the nonvariational (SAC-MET) method.

The excited states (singlet and triplet), ionized states, and electron attached states were studied by the SAC-CI expansion[3]

$$\Psi_\ell = \sum_K d_K \Phi_K \ , \qquad \Phi_K = \mathcal{P} R_K^\dagger \Psi_\ell \ , \qquad (3)$$

where d_K is an expansion coefficient. The excited function Φ_K is formed from the SAC ground state Ψ_ℓ by operating an excitation, ionization, or electron attachment operator $R_K^\dagger$, which is symmetry adapted. $\mathcal{P}$ is a projection operator $\mathcal{P} = 1 - |\Psi_\ell\rangle\langle\Psi_\ell|$. It was shown that the excited functions $\{\Phi_K\}$ thus formed span an excellent configuration space for the excited states.[3] Here, we have terminated the expansion at the second order in the coefficients

$$\Psi_\ell = \sum_K d_K \left(R_K^\dagger + R_K^\dagger \sum_I C_I S_I^\dagger - S_{K\ell}\right)|0\rangle \ , \qquad (4)$$

where $S_{K\ell} = \langle\Psi_\ell | R_K^\dagger \Psi_\ell\rangle$. As linked configurations $R_K^\dagger|0\rangle$, we have included all single and double excitations from the reference Hartree-Fock configuration $|0\rangle$ of the closed shell ground state. For the unlinked configurations $R_K^\dagger \sum_I C_I S_I^\dagger|0\rangle$, we have used the following simplifications: Since the excited, ionized, and electron attached states studied here are primarily of single excitation in nature, we have included only the single excitation operators for the $R_K^\dagger$. Since the SAC coefficients C_I of the ground state are large only for double excitations, the operators $S_I^\dagger$ included are the double excitations whose coefficients are larger than 10^{-3} in the CI including all single and double excitations. The unlinked terms thus include double excitations from all singly excited configurations $R_K^\dagger|0\rangle$, the coefficients C_I of the double excitations being transferred from the ground state SAC calculations. Since for the most part the correlations in the excited, ionized, and electron attached states should be similar to those of the ground state, this approximation should be reasonable. The SAC-CI method includes the idea of multireference CI[31] in this way.

TABLE I. Correlation energy for the ground state of formaldehyde (a.u.).

Method	Valence	Valence and Rydberg
Hartree-Fock	−113.828787	−113.830934
(1+2) CI	−0.204616	−0.206097
SAC-MET	−0.220291	−0.220293

TABLE II. Vertical excitation energy of formaldehyde calculated with the valence only basis (eV).[a]

State	Orbital picture	SAC-CI-V	SAC-CI-NV	Exptl.[b]
$^3A_2$	$n \rightarrow \pi^*$	3.69	3.72	3.5, 3.3–3.6
$^1A_2$		4.17	4.19	4.1, 4.2
$^3A_1$	$\pi \rightarrow \pi^*$	6.09	6.10	6.0, 5.6–6.2
$^1A_1$		10.87	10.90	10.7

[a]Relative to the ground state energy of −114.049078 a.u.
[b]References 20 and 22.

The SAC-CI wave function was solved by the variational (SAC-CI-V) and nonvariational (SAC-CI-NV) methods.[3] The former involves a symmetric matrix and the latter a nonsymmetric matrix. Davidson's algorithm[32] was used for a diagonalization of the symmetric matrix. For the nonsymmetric matrix we have extended Davidson's algorithm. Details will be published elsewhere.[33]

III. GROUND STATE, VALENCE, AND RYDBERG EXCITED STATES OF FORMALDEHYDE

We have used two kinds of basis set, i.e., valence only basis and valence and Rydberg basis, in order to study the nature of excited states. In Table I we have summarized the correlation energies obtained for the ground state of formaldehyde. The effect of "simultaneous collisions" of electrons as products of pair excitations included in the SAC-MET theory lowers the energy by about 0.015 a.u. in comparison with the CI including all single and double excitations (1 + 2) CI. The effect of Rydberg orbitals on the ground state energy is negligibly small, as expected.

Table II shows vertical excitation energies calculated with the valence only basis. Table III shows those calculated with the valence and Rydberg basis. $^{1,3}(n \rightarrow \pi^*)$ excitations and $^3(\pi \rightarrow \pi^*)$ excitation are well established to be valence transitions so that the results obtained by the valence only basis agree well with experiment. For the $^1(\pi \rightarrow \pi^*)$ transition there have been long controversies whether it is a valence-like transition or a Rydberg-like transition.[15–22] Experimental determination seems difficult since no experimental evidence for the $^1(\pi \rightarrow \pi^*)$ transition could be found in either the absorption or the electron scattering spectra.[10] (The value 10.7 eV in Tables II and III is due to the unpublished spectra of A. Chutjian assigned by Harding and Goddard.[22]) Theoretically, recent large scale CI calculations tend to assign it as mostly valence.[16,19,22] For example, Harding and Goddard[22] concluded that the $^1(\pi \rightarrow \pi^*)$ state is essentially (~90%) valence in character. In the present study we see that the calculations including the valence basis alone (Table II) already give a reasonable agreement

TABLE III. Vertical excitation energy of formaldehyde for valence and Rydberg excitations (eV).

State	Orbital picture	SAC–CI[a] V	SAC–CI[a] NV	Exptl.[b]	YM,[c] EOM	LD,[c] CI	HG,[c] GVB–CI
$^3A_2$	$n-\pi^*$	3.67	3.70	3.5, 3.3–3.6	3.46	3.70	3.68
$^1A_2$		4.13	4.16	4.1, 4.2	4.04	4.07	4.09
$^3A_1$	$\pi-\pi^*$	6.08	6.10	6.0, 5.6–6.2	5.29	6.21	5.95
$^1A_1$		10.80	10.83	10.7	10.10	11.05	10.77
$^3B_2$	$n-3s$	6.84	6.92	7.09, 6.7–7.0	···	6.94	7.08
$^1B_2$		6.99	7.07	7.091, 7.13	7.28	7.10	7.16
$^3B_2$	$n-3p_z$	7.76	7.83	7.92			7.99
$^1B_2$		7.91	7.99	7.97, 8.00			8.08
$^3A_1$	$n-3p_y$	7.85	7.92	8.11	···	7.81	8.05
$^1A_1$		7.92	8.00	8.14	8.15	7.86	8.09
$^3A_2$	$n-3p_x$	8.14	8.22				8.31
$^1A_2$		8.13	8.20				8.32
$^3B_1$	$5a_1(\sigma)-\pi^*$	8.49	8.52	8.50[d]			
$^1B_1$		9.46	9.49	9.0	9.19	9.30	
$^3A_2$	$1b_2(\sigma)-\pi^*$	10.78	10.80				
$^1A_2$		11.17	11.19				
$^3B_1$	$\pi-3s$	11.03	11.06			11.27	10.68
$^1B_1$		11.13	11.16	10.7	11.2	11.29	10.73
$^3B_1$	$\pi-3p_z$	11.94	11.98				11.57
$^1B_1$		12.12	12.16	11.6–11.9	12.2		11.66

[a]Calculated with the valence and Rydberg basis. Excitation energies are relative to the ground state energy of −114.051 227 a.u.
[b]References 20 and 22.
[c]YM: Yeager–McKoy (Ref. 18). LD: Langhoff–Davidson (Ref. 20). HG: Harding–Goddard (Ref. 22).
[d]Reference 11.

with experiment. Comparing Tables II and III, we see further that the effects of the Rydberg basis on the excitation energies are very small not only for the $^{1,3}(n-\pi^*)$ and $^3(\pi-\pi^*)$ transitions but also for the $^1(\pi-\pi^*)$ transition. This shows that the $^1(\pi-\pi^*)$ state is essentially valence in character, at least when it is viewed from the excitation energy.

In order to examine this problem further from a different point of view, we have shown in Table IV the dipole moments and second moments of the ground and excited states calculated with the valence only basis and with the valence and Rydberg basis. The second moment gives a measure of the size of the electron cloud. It is seen that the calculated dipole moments for the ground and $n-\pi^*$ excited states show fair agreements with experiments, though for excited states the geometry used is different from the experimental one.[10] For the $^{1,3}(n-\pi^*)$ and $^3(\pi-\pi^*)$ states the second moments are typically those of the valence states (compared with the ground state values) and the effects of the Rydberg basis are very small. For the $^1(\pi-\pi^*)$ state, however, both of the dipole moment and second moment are affected largely by the addition of the Rydberg basis set. It shows that, though the excitation energy is insensitive to the Rydberg basis, the wave function itself is not and includes Rydberg nature to some extent. Since the dipole moment changes largely from 0.81 a.u. (2.1 D) to 0.59 a.u. (1.5 D), experimental observation should be very useful. We conclude that the $^1(\pi-\pi^*)$ state has a small Rydberg character when it is measured by the dipole moment and second moment.

Table III summarizes the present results for the ver-

TABLE IV. Dipole moment and second moment of formaldehyde (a.u.).[a]

State	Orbital picture	Valence only basis $\langle z\rangle$	Valence only basis $\langle x^2\rangle$	Valence only basis $\langle y^2\rangle$	Valence only basis $\langle z^2\rangle$	Valence and Rydberg basis $\langle z\rangle$	Valence and Rydberg basis $\langle x^2\rangle$	Valence and Rydberg basis $\langle y^2\rangle$	Valence and Rydberg basis $\langle z^2\rangle$	Exptl. $\langle z\rangle$
$^1A_1$	ground	1.015	8.78	15.27	37.53	1.033	8.89	15.41	37.70	0.913[b]
$^3A_2$	$n-\pi^*$	0.502	10.57	14.23	37.31	0.491	11.50	14.58	38.00	0.508[c,e]
$^1A_2$		0.605	10.45	14.20	37.35	0.599	11.29	14.52	38.05	0.614[d,e]
$^3A_1$	$\pi-\pi^*$	0.451	9.16	15.45	38.29	0.467	9.81	15.74	38.81	···
$^1A_1$		0.809	9.67	15.75	38.59	0.590	13.58	19.24	42.66	···

[a]Results of SAC–CI–NV calculations. The second moment is calculated around the center of nuclear charge. The conversion factor between a.u. and D for dipole moment is 1 a.u. = 2.541 770 D.
[b]K. Kondo and T. Oka, J. Phys. Soc. Jpn. 15, 307 (1960).
[c]A. D. Buckingham, D. A. Ramsay, and J. Tyrrell, Can. J. Phys. 48, 1242 (1970).
[d]D. E. Freeman and W. Klemperer, J. Chem. Phys. 45, 52 (1966).
[e]The observed dipole moments of the $n-\pi^*$ excited states correspond to different geometries.

TABLE V. Dipole moment and second moment of the vertical excited states of formaldehyde calculated with the valence and Rydberg basis (a.u.).[a,b]

State	Orbital picture	Dipole moment $\langle z \rangle$	Second moment $\langle x^2 \rangle$	$\langle y^2 \rangle$	$\langle z^2 \rangle$
$^3B_2$	$n-3s$	−1.205	20.79	26.43	49.27
$^1B_2$		−1.184	22.18	27.14	49.97
$^3B_2$	$n-3p_z$	0.744	20.39	24.69	63.24
$^1B_2$		0.237	21.48	25.73	67.36
$^3A_1$	$n-3p_y$	−0.010	20.08	47.54	47.00
$^1A_1$		0.005	20.31	48.17	47.10
$^3A_2$	$n-3p_x$	0.114	43.71	24.50	46.98
$^1A_2$		0.098	43.73	24.50	46.97
$^3B_1$	$5a_1(\sigma)-\pi^*$	0.092	11.22	15.65	37.03
$^1B_1$		0.287	11.21	15.59	37.14
$^3A_2$	$1b_2(\sigma)-\pi^*$	1.378	11.70	14.34	38.70
$^1A_2$		1.311	11.66	14.29	38.49
$^3B_1$	$\pi-3s$	−0.987	19.66	27.49	48.85
$^1B_1$		−1.256	20.04	27.81	50.25
$^3B_1$	$\pi-3p_z$	0.299	18.53	25.30	64.30
$^1B_1$		0.569	20.28	27.03	66.97

[a]Calculated by the SAC–CI–NV method.
[b]For the $^{1,3}(n-\pi^*)$ and $^{1,3}(\pi-\pi^*)$ states, see Table IV.

tical excitations of formaldehyde including valence and Rydberg transitions. They were calculated with the valence and Rydberg basis. The assignments of the experimental values follow those of Harding and Goddard, who used the GVB–CI method.[22] The results due to Yeager and McKoy,[18] who used the equation-of-motion method, and those of Langhoff and Davidson,[20] who used the CI method, are also cited for comparison. It is seen that the present results show satisfactory agreement with experiments and also with the results of the previous calculations.[18,20,22] The SAC–CI–V results are consistently smaller than the SAC–CI–NV results by 0.01–0.08 eV. Van Veen, Van Dijk, and Brongersma[11] reported a new transition at 8.50 eV by threshold electron-impact spectroscopy of formaldehyde. From the present calculation we assign this peak to the $^3B_1$ $[5a_1(\sigma) - \pi^*]$ transition, which is valence in character as will be seen in Table V.

The singlet-triplet separations in excited states of formaldehyde are grouped into three classes, as Peyerimhoff and Buenker pointed out.[16] The largest one is the in-plane transition, which is the $\pi-\pi^*$ transition. The separation is as large as 4.7 eV. The smallest class includes Rydberg transitions. The calculated separations are −0.02 to 0.2 eV. An interesting one is the $^{1,3}A_2(n-3p_x)$ transitions for which the singlet state was calculated a bit lower than the triplet state. The intermediate class includes intervalence excitations involving different symmetry planes like $n-\pi^*$ and $\sigma-\pi^*$ transitions. The calculated separations are 0.4 to 1.0 eV. These differences are parallel to the magnitudes of the exchange integrals between the MO's involved, though the origin of the Hund rule is not necessarily attributed to this integral.[34]

Table V shows the dipole moments and second moments of the vertically excited states of formaldehyde (for the $n-\pi^*$ and $\pi-\pi^*$ states see Table IV). These values are obtained by the valence and Rydberg basis. Interestingly, the $^{1,3}[5a_1(\sigma)-\pi^*]$ and $^{1,3}[1b_2(\sigma)-\pi^*]$ excited states are all shown to be purely valence in nature. In comparison with Table IV, the second moments of these states are similar to those of the $^{1,3}(n-\pi^*)$ and $^3(\pi-\pi^*)$ states. The other states in Table V are typically Rydberg in nature as seen from the second moment. For the excitation into the $3p_\alpha$ orbital, the second moment increases in α direction. The dipole moment of the excited state varies largely from state to state. Especially, the dipole moments of the $^{1,3}(n-3s)$ and $^{1,3}(\pi-3s)$ states are large negative, showing shifts of electron density toward hydrogen. The singlet–triplet difference is larger in the dipole moment than in the second moment. For Rydberg excited states, the singlet state is generally a bit more diffuse than the corresponding triplet.

Table VI summarizes the results of oscillator strength for the singlet excitations of formaldehyde. They were calculated from the transition moment $\langle r \rangle_{ge}$ by

$$f = (2/3)\,\Delta E\,|\langle r \rangle_{ge}|^2 , \qquad (5)$$

with the use of the valence and Rydberg basis, except for those shown in parentheses. The present results show good agreement with experiments except for the $^1(n-3p_y)$ transition. We note that for the $^1(\pi-\pi^*)$ transition the effect of the Rydberg basis is relatively large as for the dipole moment and second moment. The $^1(n-\pi^*)$ transition is forbidden since it belongs to the A_2

TABLE VI. Oscillator strength for singlet excitations of formaldehyde (a.u.).[a,b]

State	Orbital picture	SAC–CI–V	SAC–CI–NV	Exptl.[d]	YM,[d] EOM	LD,[d] CI	HG,[d] GVB–CI
$^1A_1$	$\pi-\pi^*$	0.184(0.232)[c]	0.167(0.212)[c]		0.10	0.222	0.255
$^1B_2$	$n-3s$	0.0200	0.0203	0.028	0.02	0.034	0.006
$^1B_2$	$n-3p_z$	0.0287	0.0294	0.032			0.038
$^1A_1$	$n-3p_y$	0.0402	0.0417	0.017	0.05	0.0003	0.015
$^1B_1$	$5a_1(\sigma)-\pi^*$	0.0048	0.0048		0.002	0.0014	
$^1A_1$	$n-3d_{yz}$	0.0192	0.0186	0.015			0.0005
$^1B_1$	$\pi-3s$	0.0416	0.0423			0.00057	0.026
$^1B_1$	$\pi-3p_z$	0.0327	0.0336				0.026

[a]The transition to the state of A_2 symmetry is forbidden.
[b]Results obtained with the valence and Rydberg basis.
[c]Values in parentheses were obtained with the valence only basis.
[d]YM: Yeager–McKoy (Ref. 18). LD: Langhoff–Davidson (Ref. 20). HG: Harding–Goddard (Ref. 22).

TABLE VII. Ionization potential of formaldehyde (eV).[a]

State	Orbital picture	Koopmans	ΔSCF	SAC-CI-V[b]	SAC-CI-NV[b]	Exptl.
$^2B_2$	π^{-1}	12.12[c]	9.67[c]	10.48	10.56	10.88,[d] 10.9[e]
$^2B_1$	π^{-1}	14.67	12.66	14.66	14.70	14.38,[d] 14.5[e]
$^2A_1$	$5a_1^{-1}$	17.56		15.75	15.83	15.85,[d] 16.2[e]
$^2B_2$	$1b_2^{-1}$	19.23		17.59	17.64	16.25,[d] 17.0[e]
$^2A_1$	$4a_1^{-1}$	23.65		21.77	21.81	21.15 ± 0.15[f]

[a]Results obtained with the valence and Rydberg basis.
[b]Relative to the neutral ground state energy of −114.051 227 a.u.
[c]Reference 23.
[d]Reference 12.
[e]Reference 24.
[f]Reference 13.

symmetry. Though the GVB-CI method[22] gave excellent agreement with experiments for the transition energy, it was not so good for the oscillator strength. (The basis sets used in the GVB-CI and present calculations are similar.)

IV. IONIZED STATES AND ELECTRON ATTACHED STATES OF FORMALDEHYDE

The ionization spectrum of formaldehyde is well studied by photoelectron spectroscopy[12] and $(e, 2e)$ experiments.[13] There was an uncertainty in the assignments of the third and fourth ionization potentials in both experimental[12,13] and theoretical[24] works, though now the assignments are well established.[13] Table VII shows the present results of the SAC-CI theory and compares them with the experimental values. The basis set is the valence and Rydberg basis. For the first five ionization potentials, which are essentially of one electron processes, the present theory gives satisfactory agreement with experiment. The assignment of the spectra is consistent with the well established ones.[13] The Koopmans values are consistently too large except for a coincidence in the second ionization potential. The ΔSCF values are smaller than the experimental values. This is expected since the electron correlation in the ionized state should be smaller than that in the ground state. The SAC-CI theory includes the electron correlations of both states in a balanced way. The SAC-CI-V results are a bit smaller than the SAC-CI-NV results.

Electron transmission spectroscopy[35] has given the electron affinity of formaldehyde through the formation of a temporary negative ion.[11,14] Burrow and Michejda[14] and Van Veen, Van Dijk, and Brongersma[11] have reported electron transmission spectra at 0.66, 0.86, 1.06, 1.24, 1.41, and 1.58 eV. Burrow and Michejda assigned these peaks as being due to the vibrational levels of the $^2B_1$ ground state of H_2CO^- in which an electron is trapped in the π^* orbital. Vertical electron affinity was reported to be −0.86 eV.[11,35]

In Table VIII we have summarized the present results for the electron affinity of formaldehyde. Table IX shows the second moments of the corresponding lower-lying electron attached states. They were calculated with the valence and Rydberg basis. Due to our calculations the first lower-lying anion states will appear about 0.7–1.2 eV above the neutral ground state. Referring to Table IX, we see that these anion states are largely of Rydberg nature. Among these, the lowest $^2B_1$ state calculated at 1.02–1.05 eV above the ground state is a mixture of π^* and $3p_x$ orbitals and is relatively contracted. We assign the observed peak at −0.86 eV as corresponding to this level. Though the other peaks observed in the range −0.66 – −1.24 eV were reported to be the corresponding vibrational levels,[14] we propose a possibility

TABLE VIII. Electron affinity of formaldehyde (eV).[a]

State	Orbital picture	Koopmans	ΔSCF	SAC-CI-V[b]	SAC-CI-NV[b]	Exptl.[c]
$^2A_1$	$\infty - a_1(3s)$	−0.775	−0.742	−0.702	−0.734	−0.66
$^2B_1$	$\infty - b_1(\pi^*, 3p_x)$	−1.06	−1.05	−1.02	−1.05	−0.86
$^2B_2$	$\infty - b_2(3p_y)$	−1.21	−1.20	−1.16	−1.19	−1.06
$^2A_1$	$\infty - a_1(3p_{zC})$	−1.27		−1.20	−1.22	−1.24
$^2B_1$	$\infty - b_1(3p_x, \pi^*)$	−2.91		−2.57	−2.60	
$^2A_1$	$\infty - a_1(3p_{zO})$	−3.05		−2.93	−2.95	
...	...	...		...	...	
$^2A_1$	$\infty - a_1(C-H^*)$	−8.22		−7.72	−7.75	

[a]Calculated with the valence and Rydberg basis.
[b]Relative to the neutral ground state energy of −114.051 227 a.u.
[c]References 11 and 14. See also Ref. 34.

TABLE IX. Second moment of the lower-lying electron attached states of formaldehyde (a.u.).[a]

State	Orbital picture	$\langle x^2 \rangle$	$\langle y^2 \rangle$	$\langle z^2 \rangle$
$^1A_1$	$\infty - a_1(3s)$	−25.71	−32.33	−70.95
$^1B_1$	$\infty - b_1(\pi^*, 3p_x)$	−20.71	−20.21	−45.54
$^1B_2$	$\infty - b_2(3p_y)$	−23.70	−59.69	−56.29
$^1A_1$	$\infty - a_1(3p_{zC})$	−30.44	−36.95	−74.06
$^1B_1$	$\infty - b_1(3p_x, \pi^*)$	−33.23	−23.84	−56.65
$^1A_1$	$\infty - a_1(3p_{zO})$	−19.44	−25.95	−76.13

[a]Calculated by the SAC–CI–NV method with the valence and Rydberg basis.

that they are due to the other different anion states as shown in Table VIII.

Özkan *et al.*[25] reported the vertical π^* electron affinity of formaldehyde to be −2.22 eV by the ΔSCF method including the valence basis alone. The present calculations with the valence only basis gave the π^* electron affinity at −2.61 eV (SAC–CI–V) and −2.63 eV (SAC–CI–NV). These results are close to the second $^2B_1$ states calculated with the valence and Rydberg basis. We conclude that the observed transmission spectra at around 0.86 eV are not explained without a strong participation of the Rydberg orbitals.

For the electron attachment to the Rydberg AO's, the Koopmans theorem and the ΔSCF treatment give fairly good agreement with the SAC–CI results which include fully the correlation effects in both ground and electron attached states. This is not unexpected since an electron attached in the Rydberg orbital is far apart from the valence orbitals and the interaction between them should be small. For the electron attachment in the CH antibonding orbital, the Koopmans value is less satisfactory.

V. CONCLUSION

In the present study we have seen that the SAC and SAC–CI theories have given satisfactory results for the ground state, vertically excited states, ionized states, and electron attached states of formaldehyde. In addition to the previous calculations,[4–6] the present results show a utility of the present theory for the study of these various states. The SAC and SAC–CI theories include electron correlations in ground, excited, ionized, and electron attached states in a reasonable and balanced way. This is true for both valence and Rydberg states and for a mixed state between them. Because of the coupled cluster approach, the sizes of the matrices to be diagonalized are relatively small in both of the SAC and SAC–CI theories. Another merit is that we have used the Hartree–Fock determinant $|0\rangle$ and its MO's of the ground state throughout not only in the SAC calculations of the ground state but also in all of the SAC–CI calculations of the excited states, ionized states, and electron attached states. This is useful for theoretical and computational consistency and simplicity.

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[1]H. Nakatsuji and K. Hirao, J. Chem. Phys. 68, 2053, 4279 (1978); Chem. Phys. Lett. 47, 569 (1977); K. Ohta, H. Nakatsuji, K. Hirao, and T. Yonezawa, J. Chem. Phys. 73, 1770 (1980).
[2]K. Hirao and H. Nakatsuji, J. Chem. Phys. 69, 4535, 4548 (1978).
[3]H. Nakatsuji, Chem. Phys. Lett. 59, 362 (1978); 67, 329 (1979).
[4]H. Nakatsuji, Chem. Phys. Lett. 67, 334 (1979).
[5]H. Nakatsuji and K. Hirao, Int. J. Quantum Chem. (in press).
[6]K. Hirao and H. Nakatsuji, Chem. Phys. Lett. 79, 292 (1981).
[7]J. Paldus, J. Čízek, M. Saute, and A. Laforgue, Phys. Rev. 17, 805 (1978); M. Saute, J. Paldus, and J. Čízek, Int. J. Quantum Chem. 15, 463 (1979).
[8]I. Lindgren, Int. J. Quantum Chem. Symp. 12, 33 (1978).
[9]I. Ohmine, Chem. Phys. Lett. 72, 53 (1980).
[10]D. C. Moule and A. D. Walsh, Chem. Rev. 75, 67 (1975).
[11]E. H. Van Veen, W. L. Van Dijk, and H. H. Brongersma, Chem. Phys. 16, 337 (1976).
[12]D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, *Molecular Photoelectron Spectroscopy* (Wiley, New York, 1970).
[13]S. T. Hood, A. Hamnett, and C. E. Brion, Chem. Phys. Lett. 41, 428 (1976).
[14]P. D. Burrow and J. A. Michejda, Chem. Phys. Lett. 42, 223 (1976).
[15]R. J. Buenker and S. D. Peyerimhoff, J. Chem. Phys. 53, 1368 (1970); S. D. Peyerimhoff, R. J. Buenker, W. K. Kammer, and H. Hsu, Chem. Phys. Lett. 8, 129 (1971).
[16]S. D. Peyerimhoff and R. J. Buenker, Adv. Quantum Chem. 9, 69 (1975).
[17]J. L. Whitten and M. Hackmeyer, J. Chem. Phys. 51, 5584 (1969); J. L. Whitten, *ibid.* 56, 5458 (1972).
[18]D. L. Yeager and V. McKoy, J. Chem. Phys. 60, 2714 (1974).
[19]S. R. Langhoff, S. T. Elbert, C. F. Jackels, and E. R. Davidson, Chem. Phys. Lett. 29, 247 (1974).
[20]S. R. Langhoff and E. R. Davidson, J. Chem. Phys. 64, 4699 (1976).
[21]J. F. Gouyet and M. T. Prat, J. Chem. Phys. 64, 946 (1976).
[22]L. B. Harding and W. A. Goddard III, J. Am. Chem. Soc. 97, 6293 (1975); 99, 677 (1977).
[23]R. Colle, R. Montagnani, P. Riani, and O. Salvetti, Theor. Chim. Acta 49, 37 (1978).
[24]L. S. Cederbaum, W. Domcke, and W. Von Niessen, Chem. Phys. Lett. 34, 60 (1975); W. Domcke and L. S. Cederbaum, J. Chem. Phys. 64, 612 (1976).
[25]I. Özkan, S. Y. Chu, and L. Goodman, J. Chem. Phys. 63, 3195 (1975).
[26]S. Huzinaga, J. Chem. Phys. 42, 1293 (1965).
[27]T. H. Dunning, Jr. and P. J. Hay, In *Modern Theoretical Chemistry*, edited by H. F. Schaefer III (Plenum, New York, 1977), Vol. 3, p. 1.
[28]R. B. Lawrence and M. W. P. Strandberg, Phys. Rev. 83, 363 (1951).

[29]O. Sinanoglu, Adv. Chem. Phys. 6, 315 (1964).
[30]J. Paldus, J. Čízek, and I. Shavitt, Phys. Rev. A 5, 50 (1972).
[31]R. J. Buenker, S. D. Peyerimhoff, and W. Butscher, Mol. Phys. 35, 771 (1978).
[32]E. R. Davidson, J. Comput. Phys. 17, 87 (1975); see also W. Butscher and W. E. Kammer, *ibid.* 20, 313 (1976).
[33]K. Hirao and H. Nakatsuji (submitted for publication).
[34]E. R. Davidson, J. Chem. Phys. 42, 4199 (1965); J. Katriel, Theor. Chim. Acta 23, 309 (1972); Phys. Rev. A 5, 1990 (1972); D. A. Kohl, J. Chem. Phys. 56, 4236 (1972); J. Katriel and R. Pauncz, Adv. Quantum Chem. 10, 143 (1977).
[35]K. D. Jordan and P. D. Burrow, Acc. Chem. Res. 11, 341 (1978).

PART III, Chapter 3

Rydberg Excited States and Ionized States of NH_2 and CH_3 Radicals

I. INTRODUCTION

NH_2 and CH_3 are the simplest free radicals and their electronic structures and molecular geometries have been investigated extensively for ground and lower excited states. For higher excited states such as Rydberg excited states, however, few theoretical studies have been performed in these radicals[1-5]. In this paper we report the study of Rydberg excited states and ionized states of NH_2 and CH_3 radicals by symmetry-adapted-cluster (SAC) and SAC-CI theories[6]. These theories are suited for ground and various excited states including open-shell, ionized, and electron attached states. They have been already applied to electron and spin correlations of H_2O[7a,b], H_2CO[7c], and CH_2[7d] molecules and various doublet radicals[8] and have given satisfactory results for excitation energies, ionization potentials, electron affinities, and spin densities. In the next section, we explaine the method of calculation briefly. Calculated results and conclusion of this study are given in Sec.III and IV, respectively.

II. METHOD OF CALCULATION

The theories used, abbriviated as the SAC and SAC-CI theories, is the same as in the recent papers[6-8]. The singlet ground state wavefunctions of NH_2^+ and CH_3^+ are calculated by the SAC theory. Then the singlet and triplet excited states of NH_2^+ and CH_3^+ and the ground and excited states of NH_2 and CH_3 radicals are constructed by the SAC-CI theory. The SAC-CI wavefunction is orthogonal and orthogonal with respect to the

hamiltonian with the SAC wavefunction and it reorganizes the electron correlation effect considered by the SAC theory in the ground state. In the SAC-CI calculation, we considered up to triple excitations by the unlinked terms of R(1) of the SAC-CI and S(2) of the SAC linked operators. The basis set used here are Dunning's [3s2p/2s] CGTO[9] for valence basis and 3s, 3p, 4s, and 4p diffuse basis sets are augmented on nitrogen or carbon. The molecular geometries are fixed to the experimental geometries of doublet ground states in all the calculation. r(NH)=1.024Å and ∠HNH=103.4° for NH_2 in C_{2v} symmetry[10] and r(CH)=1.079Å for CH_3 in D_{3h} symmetry[10]. For C_{2v}, we define that z axis is parallel to the C_2 axis and the x axis is perpendicular to molecular plane. The lowest occupied orbital is fixed to be doubly occupied. Configuration selection was performed only for NH_2 with the threshold 10^{-5} a.u. in energy contribution.

III. RESULTS AND DISCUSSIONS

Vertical excitation energies to Rydberg states of NH_2 radical are given in Table I. There are no experimental data for NH_2 Rydberg excited states. The SAC-CI-V is the wavefunction obtained variationally and the SAC-CI-NV non-variationally[6c]. Here, we calculate the excitation from a singly occupied orbital to virtual orbitals. The electronic configurations of the Hartree Fock (HF) wavefunctions are

$(1a_1)^2 (2a_1)^2 (1b_2)^2 (3a_1)^2 (1b_1)^1 (3s)^0 (3py)^0 (3px)^0 (3pz)^0$ ... for

NH_2,

and

$(1a_1')^2(2a_1')^2(1e')^4(1a_2'')^1(3s)^0(3px,y)^0(3pz)^0$ ... for CH_3.

We cited the result of multi-reference CI (MR-CI) of Peyerimhoff et al.[1] as reference data. The first and second excited states are assigned to $^2A_1$ and $^2B_2$ respectively. These lower states correspond to the valence excited states where one electron excites from doubly occupied orbitals, $3a_1$ and $1b_2$, respectively, to halfly occupied orbital $1b_1$ in the HF picture. The $^2A_1$ state is the first Rydberg state of NH_2 radical. Calculated results are close to the results of MR-CI wavefunction.

For Rydberg states of CH_3, there are a few of theoretical studies as shown in Table II. The study by GVB-CI[3] is, to the best of our knowledge, only one investigation for Rydberg states of CH_3 by a correlated wavefunction. The excitation energy to $^2A_1'$ state by the SAC-CI theory agreed satisfactorily with the experimental result. The $^2E'$ state, which corresponds to valence excited state $(1a_1')^2(2a_1')^2(1e_1')^3(1a_1'')^2$ in the orbital picture, is assigned to the next high state of $^2E'$ which corresponds from $1a_2''$ to 3px, 3py in the previous study with HF wavefunction[4]. However we did not calculate this state since only the excitations from the $1a_2''$ orbital were considered in this study.

Vertical ionization potentials of NH_2 and CH_3 radicals are given in Table III and IV, respectively. The most stable state of NH_2^+ is $^3B_1$. The calculated ionization energies of NH_2

to this state is rather small in comparison with the experimental values[2a]. Calculated singlet-triplet separation in $^{1,3}B_1$ excited state is 2.70eV and it is fairy good in comparison with the experimental value, 2.27eV. The ionization potentials of CH_3 are also slightly small in comparson with the experimental results. The $^{1,3}E''$ states are expected to exhibit the Jahn-Teller splitting. In this study, however, we investigated only the vertical excitation to these degenerate states.

IV. CONCLUSION

The Rydberg excited states and ionized states of NH_2 and CH_3 were investigated by the SAC and SAC-CI theories. There are few experimental and theoretical studies for Rydberg excited states or ionization energies though these are the most basic free radicals. For the vertical excitations to Rydberg states of NH_2 radical, the present result agreed well with the results of MR-CI theory[1]. For the Rydberg excited state of CH_3, the SAC and SAC-CI theories have given satisfactory result in comparison with the experimental result. The ionization energies of NH_2 and CH_3 were calculated rather small and, for excitation energies of CH_3 radical, present theories gave good result.

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REFERENCES

1. S.D.Peyerimhoff and R.J.Buenker, Can.J.Chem. 57, 3182 (1979).

2. (a) S.J.Dunlavey, J.M.Dyke, N.Jonathan, and A.Morris, Mol.Phys. 39, 1121 (1980). (b) J.Dyke, N.Jonathan, E.Lee, and A.Morris, J.Chem.Soc.Farad. Trans.II 72, 1385 (1976).

3. G.T.Surratt and W.A.Goddard III, Chem.Phys. 23, 39 (1977).

4. R.McDiarmid, Theoret.Chim.Acta(Berl.) 20, 282 (1971).

5. Y.Ishikawa and R.C.Binning Jr., Chem.Phys.Lett. 40, 342 (1976).

6. (a) H.Nakatsuji and K.Hirao, J.Chem.Phys. 68, 2053 (1978). (b) H.Nakatsuji, Chem.Phys.Lett. 59, 362 (1978). (c) H.Nakatsuji, Chem.Phys.Lett. 67, 329, 334 (1979).

7. (a) H.Nakatsuji and K.Hirao, Int.J.Quantum.Chem. 20, 1301 (1981). (b) K.Hirao and H.Nakatsuji Chem.Phys.Lett. 79, 292 (1981). (c) H.Nakatsuji, K.Ohta, and K.Hirao, J.Chem.Phys. 75, 2952 (1981). (d) H.Nakatsuji and T.Yonezawa, Chem.Phys.Lett., in press.

8. H.Nakatsuji, K.Ohta, and T.Yonezawa, to be published.

9. T.H.Dunning, Jr. and P.J.Hay, in Modern Theoretical Chemistry , edited by H.F.Schaefer III (Plenum, NY, 1977), vol.3, p.1.

10. G.Herzberg, Electronic Spectra of Polyatomic Molecules (Van Nostrand, Princeton, 1967).

Table I. Vertical excitation energies of NH_2 (eV).

State	Excitation	SAC-CI-V	SAC-CI-NV	Peyrimhoff et al.[a]
$^2A_1$	$3a_1 - 1b_1$			2.161
$^2B_2$	$1b_2 - 1b_1$			6.639
$^2A_1$	$1b_1 - 3s$	7.22	7.29	7.690
$^2B_2$	$1b_1 - 3py$	9.06		
$^2A_1$	$1b_1 - 3pz$	9.56	9.65	

a. Reference 1.

Table II. Vertical excitation energies of CH_3 (eV).

State	Excitation	SAC-CI-V	Exptl.[a]	GVB-CI[b]	ΔSCF
$^2A_1'$	$1a_2'' - 3s$	5.73	5.728	6.07	5.40[c], 5.453[d]
$^2E'$	$1a_2'' - 3px,y$	6.99			7.60[c], 7.731[d]
$^2A_2''$	$1a_2'' - 3pz$	7.18			

a. Reference 10.

b. Reference 3.

c. Reference 4.

d. Reference 5.

Table III. Vertical ionization potentials of NH_2 (eV).

State	Ionization	SAC-CI-V	SAC-CI-NV	Exptl.[a]	ΔSCF[a]
$^3B_1$	$3a_1 - \infty$	10.85	10.84	12.00	10.37
$^1A_1$	$1b_1 - \infty$	12.06	11.93	12.45	11.62
$^1B_1$	$3a_1 - \infty$	13.55	13.54	14.27	12.88
$^3A_2$	$1b_2 - \infty$	16.56	16.51		15.50
$^1A_2$	$1b_2 -$	17.80	17.75		16.98

a. Reference 2(a).

Table IV. Vertical ionization potentials of CH_3 (eV).

State	Ionization	SAC-CI-V	Exptl.[a]	ΔSCF[a]
$^1A_1'$	$1a_2 - \infty$	8.27	9.843	9.78
$^3E''$	$1e' - \infty$	13.53	14.76	14.71
$^1E''$	$1e' - \infty$	14.46	16.10	15.93
$^3E'$	$1e' - \infty$ $1a_2'' - 3s$	22.57		

a. Reference 2(b).

CHAPTER 4

SUMMARY

Here we investigated the electron correlation of ground state, valence and Rydberg excited states, and ionized states of H_2CO, NH_2, and CH_3 molecules by the SAC and SAC-CI theories. For formaldehyde, in chapter 2, calculated excitation properties have given satisfactory agreement with the results of experiments and various excited states have been assigned. The mixing of valence and Rydberg excitations in the $^1A_1$ ($\pi - \pi^*$) excited state has also been investigated. From the energetical point of view, this state is found to be valence in character. However, calculated second moment in this state, which gives a measure of the size of the electron cloud, has shown a small Rydberg character. For the Rydberg excited states, ionized states of NH_2 and CH_3 radicals, the SAC and SAC-CI theories have also given reasonable results in comparison with the experiments and the previous theoretical works. From these results, it has been confirmed that the SAC and SAC-CI theories can be applied to various electronic states, such as singlet and triplet excited states, Rydberg states, ionized states, eletron attached states, and radical states, systematically and they give quantitative results in comparison with experimental values.

PART IV

APPLICATION OF THE PSEUDO-ORBITAL THEORY TO THE GEOMETRIES AND hfs CONSTANTS OF DOUBLET RADICALS

CHAPTER 1

INTRODUCTION

In the previous chapters in this thesis, the reliability and applicability of the SAC and SAC-CI theories have been proved in various electronic states. In those studies, the PO theory which is one of the simplest application of the SAC expansion theory has given fairly good result for spin correlation problems although the coupling effect with the electron correlation is not always small. Then the careful application of the PO theory to the spin correlation problem should give reasonable results with its simplicity in the calculation. We studied the spin density and molecular geometry of CH_3, SiH_3, and GeH_3 radicals in chapter 2. Molecular geometries of these radicals have been studied by the simple s-character estimation from observed ESR specra and SiH_3 is reported to be most pyramidal[1]. GeH_3 is, however, thought to be most pyramidal by qualitative consideration based on the electrostatic force (ESF) theory[2]. We optimized geometries of these radicals by the PO theory. The spin-polarization in the multi inner shells and the effect of molecular vibration for the spin density and molecular structure are also studied. In chapter 3, we studied the Jahn-Teller (J-T) distortion of cation radicals of cyclopropane, cyclobutane, and cyclopentane. Since these are σ radicals, interesting spin distributions are obtained reflecting the distorted carbon or the C-H bonds by the J-T effects sensitively.

References

1. R.L.Morehouse, J.J.Christiansen, and W.Gordy, J.Chem.Phys. 45, 1751 (1966); G.S.Jackel, J.J.Christiansen, and W.Gordy, J.Chem.Phys.47, 4274 (1967); G.S.Jackel, and W.Gordy, Phys.Rev. 176, 443 (1968).

2. H.Nakatsuji, J.Am.Chem.Soc., 95, 345, 354 (1973).

PART IV, Chapter 2

Molecular Structures and Spin Correlations of CH_3, SiH_3, and GeH_3 Radicals

1. INTRODUCTION

The hyperfine splitting (hfs) constants of the AH_3 radicals, including the IV-the group elements as the central atom A, have been systematically studied experimentally[1] and, for methyl and sillyl radicals, several ab initio studies have been performed[2,3]. The molecular structures of these AH_3 radicals, especially the out-of-plane angles have been discussed on the basis of the central atom s-character obtained from e.s.r. measurements[1]. Gordy et al. reported the out-of-plane angles to be 0°, 15.1°, and 13.1° for CH_3, SiH_3, and GeH_3, respectively. This sequence of pyramidality, however, seems to be rather irregular from the general consideration in the Walsh rule[4] and the electrostatic force (ESF) theory[5]. Due to the qualitative consideration based on the ESF theory, the out-of-plane angle will increase as the central element A becomes heavier in the IV-th group elements, the gap being large between C and Si and small among Si, Ge, and Sn.

In this study we perform ab initio calculation of the molecular geometry and hfs constant of these AH_3 (A; C, Si, Ge) radicals. The hfs constant has been calculated by the pseudo-orbital (PO) theory[6]. The PO theory is a new open-shell orbital theory based on the symmetry-adapted-cluster (SAC) expansion theory[6] and includes open-shell spin-correlation effects correctly in comparison with the conventional open-shell orbital theories such as the unrestricted HF (UHF)[7] and the spin-extended (SE) HF[8] theory. In the previous studies[9], we applied the PO theory to the calculations of hfs constants of various open-shell atoms

where $S^{+}_{P,tk}$ is a spin-adapted excitation operator which generates a spin-polarization configuration,

$$S^{+}_{P,tk}|0> = 3^{-1/2}\{2^{-1/2}||\phi_1\alpha\phi_1\beta \,..\, \phi_t\phi_k(\alpha\beta + \beta\alpha)..\, \phi_q\alpha\phi_q\beta\phi_m\alpha|| + 2^{1/2}\,||\phi_1\alpha\phi_1\beta \,..\, \phi_k\alpha\phi_t\alpha \,..... \phi_q\alpha\phi_q\beta\phi_m\beta||\}, \quad (4)$$

on applying the reference wavefunction $|0>$, which is restricted HF (RHF) wavefunction. The suffixes k, m, and t denote doubly occupied, singly occupied, and unoccupied orbitals, respectively. $\mathcal{O}_{1/2}$ is the projection operator on to the doublet spin space.

We have calculated spin density correct to second order in the coefficients.

$$\rho(r) = \rho_{SD}(r) + \rho_{SP}(r), \quad (5)$$

$$\rho_{SD}(r) = N_0<0|\hat{\rho}(r)|0> = N_0|\phi_m(r)|^2, \quad (6)$$

$$\rho_{SP}(r) = \rho_{SP1}(r) + \rho_{SP2}(r) = N_0\{2\sum_I C_I<0|S_I\hat{\rho}(r)|0> + \sum_{IJ}\sum C_IC_J<0|S_I\hat{\rho}(r)S^{+}_J|0>\}, \quad (7)$$

where N_0 is a normalization factor and I denotes the set of indices, (P,tk) of the wavefunction (1). $\hat{\rho}$ denotes a normalized spin density operator. The subscripts SD and SP mean spin-delocalization and spin-polarization contribution, respectively[11]. The ρ_{SD} arises from the delocalization of the radical orbital ϕ_m and it is always positive or zero. The ρ_{SP} arises from the spin-polarization correction to the RHF wavefunction by the PO theory. It is either positive or negative. The ρ_{SP1} is the first-order contribution and the ρ_{SP2} is the

second-order contribution. The hfs constant a^N in gauss unit and the spin density $\rho(r_N)$ in atomic unit are connected by the following relation,

$$a^N = (8\pi/3)(g_e/g_0)g_N\beta_N\rho(r_N), \tag{8}$$

in standard notation[9]. Specifically a^H = 1592.2 ρ(H), a^C = 400.4 ρ(C), a^{Si} = -316.3 ρ(Si), and a^{Ge} = -55.54 ρ(Ge).

The basis set used in this study are contracted gauss type functions (CGTO) of double zeta quality. For carbon we used Huzinaga's (9s5p) set[12] contracted to (4s2p) set[2(d)] and for hydrogen (4s) contracted to (2s) [9] with the scale factor 1.2. The silicon basis is Dunning's (6s4p) CGTO[13]. For germanium we used (14s10p6d) set contracted to (6s5p2d) [14].

The vibrational effects on the geometry and hfs constants were studied as follows. The expectation value of an operator $\hat{\Omega}(Q)$, which is a function of nuclear coordinate, for the vibrational wavefunction $\chi(Q)$ is obtained from the equation,

$$\overline{\Omega} = \int\int\cdots\int \chi^*(Q)\ \hat{\Omega}(Q)\ \chi(Q)\ dQ_1 dQ_2 \cdots dQ_{3N-6}, \tag{9}$$

where Q is a set of 3N-6 normal coordinates, $\{Q_k\}_{k=1,3N-6}$. In this study, we constrained the molecular geometry of AH_3 to C_{3v}. Then the internal coordinates are out-of-plane angle θ and bond length r(AH). The hfs constant of AH_3 radical, especially for the central element A, is a sensitive function of the out-of-plane angle but not sensitive to the variation of the bond length [3,10]. Here we discuss mainly the vibrational

effect on the hfs contant of the central element A and the molecular pyramidality. Then we consider only the bending vibration and neglect the effect of the stretching mode, i.e., we approximate the hfs constant to be represented as a function of only the out-of-plane angle θ, i.e., $a(\theta)$. Then Eq.(9) is approximated effectively as

$$\bar{a} = \int \chi^{*}(\theta)\ a(\theta)\ \chi(\theta)\ d\theta. \tag{10}$$

The out-of-plane angle was also averaged by the equation,

$$\bar{\theta} = \int \chi^{*}(\theta)\ |\theta|\ \chi(\theta)\ d\theta. \tag{11}$$

The vibrational wavefunction $\chi(\theta)$ was calculated on the basis of the one dimensional adiabatic potential obtained from the PO theory. The potential was expanded into polynomial function of the out-of-plane angle θ by the least square fitting method. The wavefunction of molecular vibration was approximated by a linear combination of harmonic oscillators and their expansion coefficients were determined variationally. The exponential factors of the harmonic oscillators were determined by minimizing the difference

$$|\langle H^2 \rangle - \langle H \rangle^2|. \tag{12}$$

The reduced mass, for the approximate inversion coordinate θ, is a function of θ itself. However, we can fix it, to a good approximation, to the value of the planar geometry, since the

angular dependence of the reduced mass is small.

3. ENERGY AND hfs CONSTANT ADIABATIC POTENTIAL

The optimized geometries of CH_3, SiH_3, and GeH_3 radicals are given in Table 1. The out-of-plane angles of SiH_3 and GeH_3 are calculated to be 16.1° and 18.4°, respectively, which are larger than those estimated from the e.s.r. measurement. The decrease in the out-of-plane angle from SiH_3 (θ=15.1°) to GeH_3 (θ=13.1°) estimated from the e.s.r. measurement[1] was not reproduced.

Fig.1(a), Fig.1(b), and Fig.1(c) show the adiabatic potential for the out-of-plane mode. The bond length was kept fixed to the optimized value shown in Table 1. The potential curve of CH_3 is a single well as shown in Fig.1(a). The energy lowering, due to the spin-correlation correction by the PO theory, is 4.9 kcal/mol at planar structure and decreases as the out-of-plane angle increases. The effect of the spin-correlation was found to be largest at the planar structure commonly for these AH_3 radicals. (This trend is understood by a simple orbital interaction picture which will be shown below.) The adiabatic potentials for SiH_3 and GeH_3 are double well as shown in Fig.1(b) and Fig.1(c). The energy lowering due to the spin-correlation is 3.9 kcal/mol for SiH_3 and 5.3 kcal/mol for GeH_3 at planar structure. The inversion barrier is thus reduced to 3.0 kcal/mol for SiH_3 and 5.8 kcal/mol for GeH_3. Because of the small inversion barriers, we except large vibrational effect. Quantitative estimates will be given below.

hfs CONSTANT

In Table 1, we show the hfs constants calculated by the PO theory at the optimized geometry. For CH_3 and SiH_3 radical fairly good results are obtained. On the other hand, the result of GeH_3 is rather poor. The hfs constant of Ge was calculated about twice as large as the experimental value.

The change of hfs constants versus the out-of-plane angle are shown in Fig.2(a), Fig.2(b), and Fig.2(c). In these figures, SD is the spin-delocalization contribution and SP is the spin-polarization contribution. Total hfs is the sum of these two contributions. Though the inversion potentials have different features, such as single or double well, the hfs curves are very similar in these radicals. Since the hfs constant is a direct reflection of the electronic wavefunction, these AH_3 radicals are considered to have very similar electronic and spin structures.

For the central element A, the SD contribution is very sensitive to the out-of-plane angle and increases rapidly. At the planar structure, these radicals become π radicals ($^2A''$) and the total hfs constants are determined only by the SP contribution. Though the SP contribution is less sensitive to the out-of-plane angle than the SD contribution, it also varies with the out-of-plane angle and becomes largest at the planar geometry. This is the same trend as in the case of the spin-correlation correction for the energy in the previous paragraph.

This trend in the spin-correlation effect for the AH_3 radicals is understood qualitatively by a simple orbital picture

based on the first-order perturbation theory. The first-order SP contribution, SP1 in Eq.(7), comes from the matrix element of the RHF reference wavefunction and the spin-polarized configuration $S^{+}_{P,tk}|0>$. The expansion coefficient of $S^{+}_{P,tk}|0>$ can be expressed approximately by the first-order perturbation theory as,

$$C_{P,tk} = <0|HS^{+}_{P,tk}|0>/(E_0 - E_{P,tk})$$
$$= -(3/2)^{1/2}(km|mt)/(E_0 - E_{P,tk}). \qquad (13)$$

Thus, the SP1 contribution depends on the exchange type integral (km|mt) which represents the interaction between the doubly occupied orbital k and the unoccupied orbital t through the radical orbital m. In Fig.3, we showed a schematic picture of a_1-HOMO(k), a_1-LUMO(t) and the radical orbital m (SOMO). The most important spin-poralized configuration is constructed by these three orbitals. When the out-of-plane angle increases and the s-p hybridization ratio in these orbitals becomes larger, the differential overlaps between k and m and m and t become smaller, as expected from Fig.3, and the exchange integral (km|mt) decreases. This is the reason why the spin-correlation effect decreases as the out-of-plane angle increases in these AH_3 radicals.

For the hfs constant of hydrogen, the SD contribution is less sensitive to the out-of-plane angle than that of the central element A. The SP contribution curve is almost parallel with that of the central element and it is also largest at the planar geometry.

4. EFFECT OF MOLECULAR VIBRATION

Since the hfs constants depend largely on the out-of-plane angle θ, and the inversion barriers are small (0 ~ 6 kcal/mol), the effect of the bending vibration is considered to be very important for the hfs constants, especially for the central element A. In this section, we average the calculated hfs constants over the zero-point vibrational wavefunction. We also consider the vibrational effect on the out-of-plane angle of these AH_3 radicals. The effects of vibration on the hfs constants of AH_3 radicals are calculated for the zero-point vibrational level of bending mode and they are given in Table 2. The changes in the hfs constants are 9.6G, 9.0G, and 4.2G for C, Si, and Ge, respectively. The carbon hfs constant became larger by the contribution from the more pyramidal structure since the equilibrium geometry of CH_3 is planar. For SiH_3 and GeH_3, however, their equilibrium geometry is pyramidal. Then, the contribution from the more pyramidal structure makes the hfs values of Si and Ge more negative and that from the planar structure makes them less negative. In this study, the contribution from the planar structure was larger than that from the pyramidal structure and the averaged hfs values of Si and Ge became less negative. On the other hand, the vibrational effect on the hydrogen hfs constant is small and is about 2G for these radicals.

In order to study the effect of molecular vibration on the out-of-plane angle itself, we calculated the most probable out-of-plane angle by equation (9). The calculated results are

given in Table 2. For these three radicals, the out-of-plane angle changed about 1 degree by averaging with the vibrational wavefunction. The out-of-plane angle of CH_3 is calculated 4.13° and it is the mean-square amplitude. The equilibrium geometry is, of course, planar. For both of SiH_3 and GeH_3 the optimized geometries are more pyramidal than those of the experimental results. When we consider the effect of vibration, the SiH_3 and GeH_3 became more planar and the out-of-plane angle of SiH_3 agreed with the experimental value, 15.1°. Again, the decrease in the pyramidality from SiH_3 to GeH_3 estimated from the e.s.r. measurement was not reproduced in these most probable geometries.

5. SHELL STRUCTURE OF SPIN-POLARIZATION EFFECT

We analyze here the spin-polarization (SP) term in the hfs constant as the sum of the shell contributions. For heavier elements like Si and Ge, which have multi-shell structure, the contributions of inner shells are of interest. In Table 3, we showed the shell structure of the first-order spin-polarization contribution ρ_{SP1} for the central element at the equilibrium geometry. It is found that all of the 1s-shells give negative contributions and that the total spin-polarization effect is primarily determined by two shells, valence shell and the next lower shell. The contribution of deeper shells in SiH_3 and GeH_3 seems to be small and canceling. In these AH_3 radicals, the nature of the radical orbital changes largely when the out-of-plane angle changes. Thus, the inner shell contribution to the spin-polarization effect will change largely through the

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coupling with the radical orbital. In Fig.4(a), 4(b), and 4(c), we plotted the shell contribution versus the out-of-plane angle for CH_3, SiH_3, and GeH_3, respectively. The 1s-inner shell and 2s-valence shell of CH_3 are spin-polarized by the odd electron on the central carbon. The 2s-valence shell contribution decreases rapidly as the out-of-plane angle increases. This is the result of rapid decrease of orbital interaction between a_1-HOMO and a_1-LUMO through the radical orbital, the same reason as for the energy lowering due to the spin-correlation discussed in Sec.3. The contribution of the 1s-shell, which is nearly spherical and localized to carbon, does not change so rapidly as the 2s-shell contribution and it increases monotonously as shown in Fig.4(a). The change of the SP1 contribution of Si in SiH_3 radical is also shown in Fig.4(b). 3s-shell is valence shell and its contribution decreases rapidly. It is interesting that, though the potential curve is very different between CH_3 and SiH_3 radical, the valence shell spin-polarization curve is very similar. The inner shell contribution, 1s- and 2s-shell in SiH_3, increases monotonously as in the case of CH_3 radical. For these two radicals, the shell structure of the spin-poralization varied largely with the change in the out-of-plane angle and inner shell contribution is not always small. The shell analysis for GeH_3 is given in Fig.4(c). The valence shell contribution decreases very rapidly. The inner shell contribution, however, is relatively small and does not change so much as in the case of CH_3 or SiH_3.

6. CONCLUSION

Structures and hfs constants of CH_3, SiH_3, and GeH_3 radicals have been calculated by the pseudo-orbital (PO) theory. In these IV-th group AH_3 radicals, SiH_3 was reported to be the most pyramidal through the s-character estimation from e.s.r. measurement. It was found in this study, however, that GeH_3 is most pyramidal and the decrease in the out-of-plane angle from SiH_3 to GeH_3 was not reproduced even if we consider the effect of molecular vibration. hfs constants of CH_3 and SiH_3 calculated by the PO theory were in fair agreement with the experimental values, but for GeH_3 rather poor result was obtained in this calculation. The small inversion barrier and the strong dependence of the hfs constant of the central element A on the out-of-plane angle caused large vibrational effect in these AH_3 systems. The hfs constant of the central element A changed by 9.6G, 9.0G, and 4.2G for C, Si, and Ge elements, respectively. Finally, the spin-polarization effect, considered by the PO theory, has been decomposed into valence and inner shell contributions. For CH_3 and SiH_3, the inner shell spin-polarization effect for the hfs constants of the central element is not always small and varied largely with the change in the molecular pyramidality. For GeH_3, the inner shell contribution is negligibly small and does not change so large as in the case of CH_3 or SiH_3 radical.

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References

[1]. Morehouse, R. L., Christiansen, J. J., and Gordy, W., 1966, J. Chem. Phys., 45, 1751.; Jackel, G. S., Christiansen, J. J., and Gordy. W., 1967, J. Chem. Phys., 47, 4274.; Jackel, G. S., and Gordy, W., 1968, Phys., Rev. 176, 443.

[2]. (a) Chang, S. Y., Davidson, E. R., and Vincow, G., 1970, J. Chem. Phys., 52, 1740. (b) Konishi, H., and Morokuma, K., 1972, J. Am. Chem. Soc., 94, 5603. (c) Millie, P., Levy, B., Berthier, G., 1972, Int. J. Quantum Chem., 6, 155. (d) Ellinger, Y., Rassat, A., Subra, R., and Berthier, G., 1975, J. Chem. Phys., 62, 1. (e) Wirsam, B., 1973, Chem. Phys., Lett., 18, 578. (f) Aarons, L. J., Hiller, I. H., and Guest, M. F., 1974, J. Chem. Soc. Farady II, 70, 167.

[3]. (a) Barone,V., Douady, J., Ellinger, Y., Subra, R., and Pauzat, F., 1979, Chem. Phys., Lett., 65, 542.; (b) Ellinger, Y., Pauzat, F., Barone, V., Douady, J., and Subra, R., 1980, J. Chem. Phys., 72, 6390.

[4]. Walsh, A. D., 1953, J. Chem. Soc., 2296.

[5]. Nakatsuji, H., 1973, J. Am. Chem. Soc., 95, 345, 354.

[6]. Nakatsuji, H., and Hirao, K., 1978, J. Chem. Phys., 68, 2053.

[7]. Pople, J. A., and Nesbet, R. K., 1954, J. Chem. Phys., 22, 571.

[8]. Lowdin, P.-O., 1955, Phys. Rev., 97, 1490, 1509.; Pauncz, R., "Alternant Molecular Orbital Method", (Saunders, Philadelphia, PA, 1967); Kaldor, U., 1968, J. Chem. Phys., 48, 835.

[9]. Nakatsuji, H., and Hirao, K., 1977, Chem. Phys., Lett., 47, 569.; Nakatsuji, H., and Hirao, K., 1978, J. Chem. Phys., 68, 4279.; Ohta, K., Nakatsuji, H., Hirao, K., and Yonezawa, T., 1980, ibid. 73, 1770.

[10]. Beveridge, D. L., and Miller, K., 1968, Molec. Phys., 14, 401.; Sutcliffe, B. T., and Gaze, C., 1978, Molec. Phys., 35, 525.

[11]. Nakatsuji, H., Kato, H., and Yonezawa, T., 1969, J. Chem. Phys., 51, 3175.

[12]. Huzinaga, S., 1965, J. Chem. Phys., 42, 1293.

[13]. Dunning, T. H., and Hay, P. J., in: "Method of Electronic Structure Theory" (H. F. Schaefer III Ed.) Vol.3 p. 1. Plenum Press, NY. 1977).

[14]. Eades, R. A., and Dixon, D. A., 1980, J. Chem. Phys., 72, 3309.

Table 1. Structure and hfs constant of AH_3 radicals without vibrational averaging[a].

		CH_3	SiH_3	SiH_3[b,g]	GeH_3
opt. geom.	r(Å)	(1.079)[c]	1.472	1.477	1.554
	θ[d] (deg.)	0.0	16.1	16.4	18.4
hfs	A (gauss)	39.4	-173.8	-177.6	-156.3
	H (gauss)	-26.5	-10.1	-1.0	8.4
inversion barrier (kcal/mol)		0.0	3.0	4.0	5.8
exptl.[e] geom.	r(Å)	1.079	1.48(SiH_4)		1.53(GeH_4)
	θ (deg.)	0.0	15.1		13.1
hfs	A (gauss)	38.3	190		75±3
	H (gauss)	23.0	8.1±0.5		15±2
total energy (a.u.)					
planar geometry (θ=0°)	RHF	-39.5373	-290.5586	-290.5571[f]	-2073.9163
	PO	-39.5451	-290.5648	-290.5616[f,g]	-2073.9248
opt. geom.	RHF	-----	-290.5673	-290.5663[g]	-2073.9307
	PO	-----	-290.5696	-290.5680[g]	-2073.9341

a. Result of pseudo-orbital (PO) theory.

b. Result of double zeta CGTO in reference [3(a)].

c. Experimental bond length from G. Herzberg, "Electronic Spectra of Polyatomic Molecules" (Van Nostrand, Princeton, 1967).

d. Out-of-plane angle.

e. Reference [1].

f. r(Si-H) = 1.464Å in reference [3(a)].

g. Result of first-order-perturbation theory.

Table 2. Bending vibrational effect on the hfs constant and molecular structure[a].

		CH_3	SiH_3	GeH_3
averaged hfs (gauss)	A	49.0(9.6)	-164.8(9.0)	-152.1(4.2)
	H	-24.8(1.7)	-12.3(-2.2)	6.9(-1.5)
most probable out-of-plane angle θ^b(deg.)		4.13(4.13)	15.1(-1.0)	17.7(-0.7)
exptl.[c] θ^b(deg.)		0.0	15.1	13.1
exptl.[c] hfs				
	A (gauss)	38.3	190	75 ± 3
	H (gauss)	23.0	8.1 ± 0.5	15 ± 2

a. Calculated by zero-point vibration wavefunction in the bending mode. The effect of vibration is given in the parentheses.
b. Out-of-plane angle.
c. Reference [1].

Table 3. Shell analysis for the SP1 contribution of spin density at the central element in equilibrium geometry. ($bohr^{-3}$)

	CH_3	SiH_3	GeH_3
Total	0.0867	0.1456	0.1932
	2s(0.2038)	3s(0.0854)	4s(0.1982)
	1s(-0.1171)	2s(0.0861)	3s(-0.0080)
		1s(-0.0258)	2s(0.0035)
			1s(-0.0005)

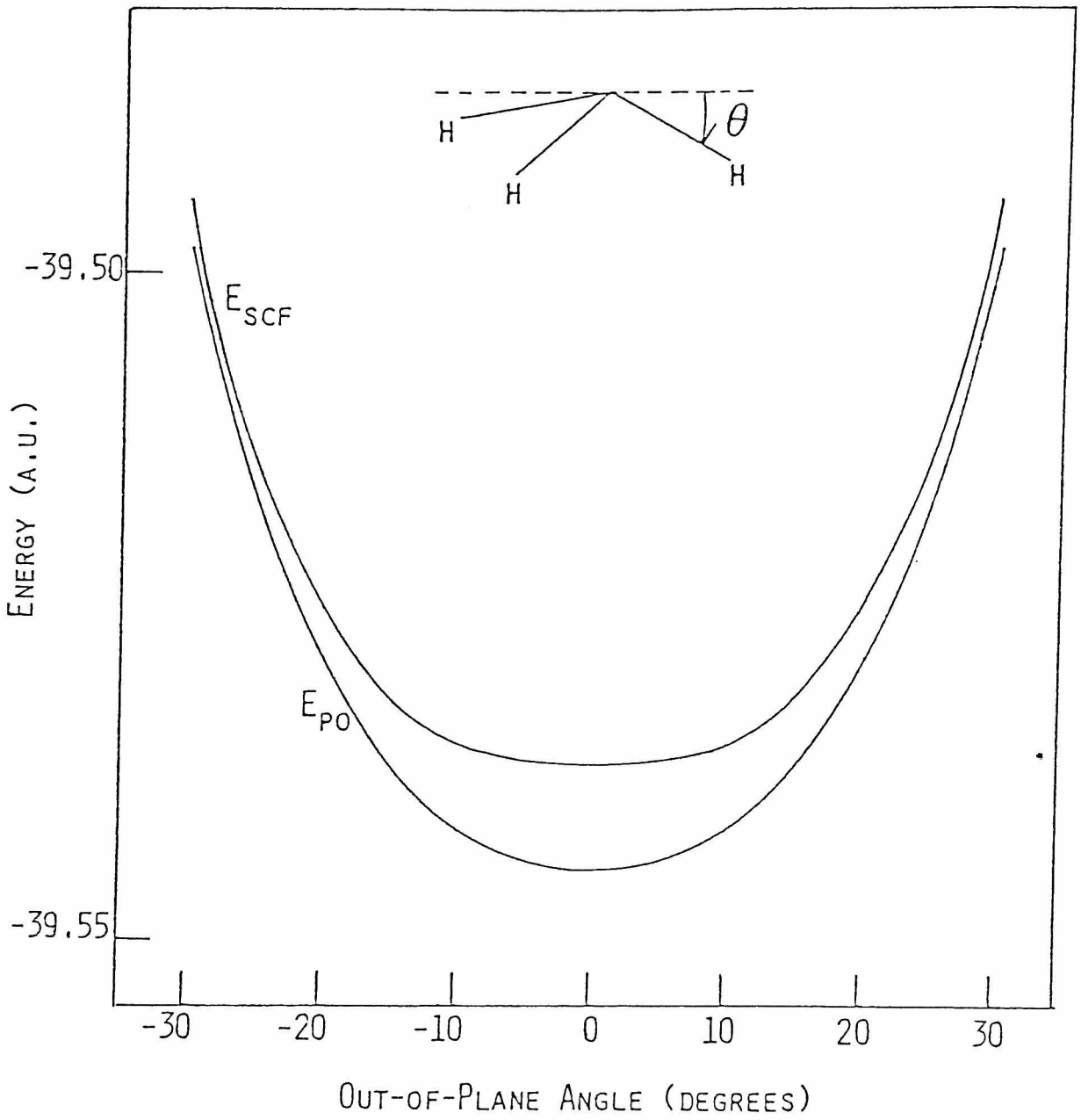

Figure 1(a). SCF (E_{SCF}) and pseudo-orbital (E_{PO}) energies for CH_3 versus out-of-plane angle. Bond length is 1.079 Å.

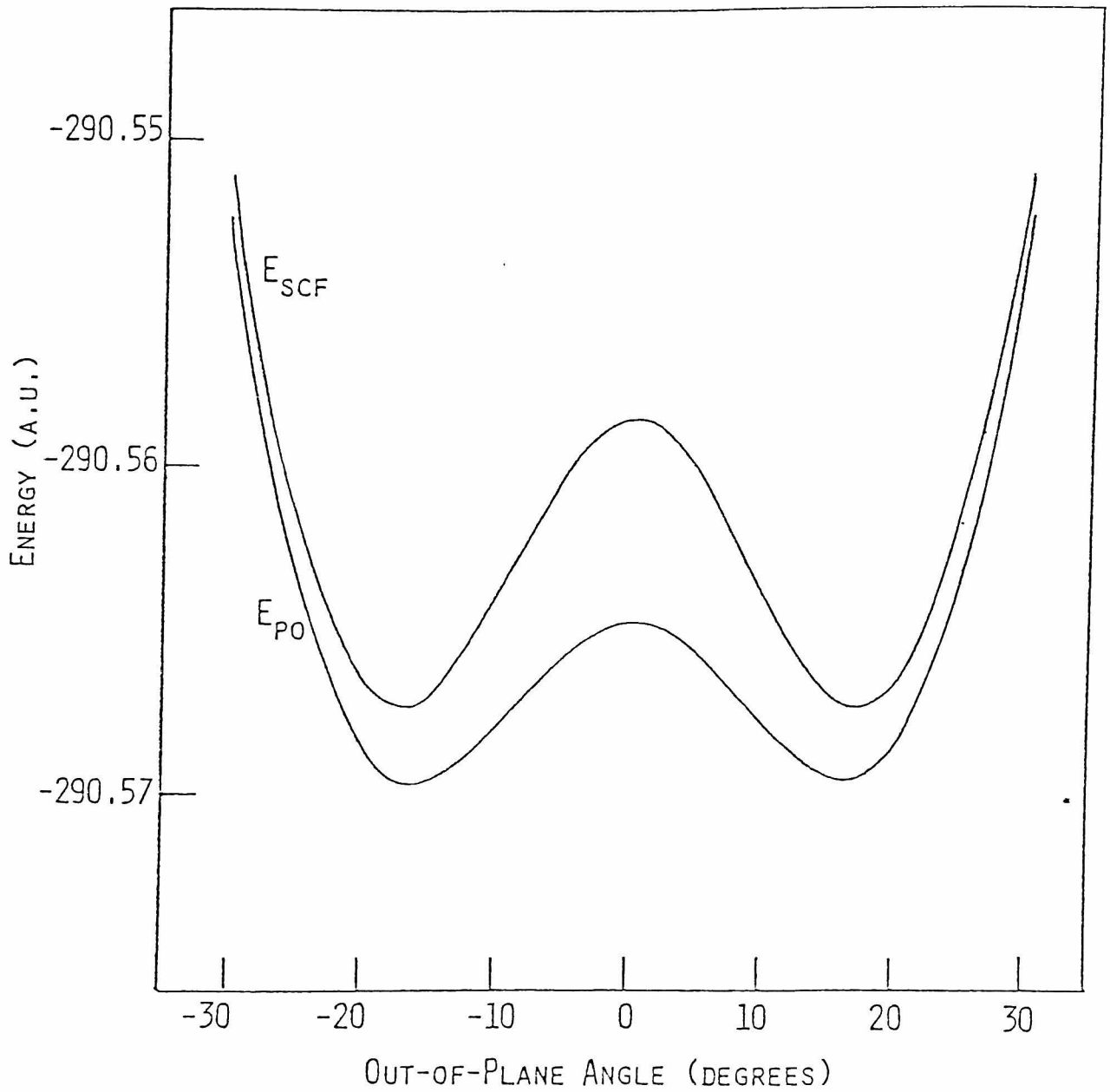

Figure 1(b). SCF (E_{SCF}) and pseudo-orbital (E_{PO}) energies for SiH_3 versus out-of-plane angle. Bond length is 1.472 Å.

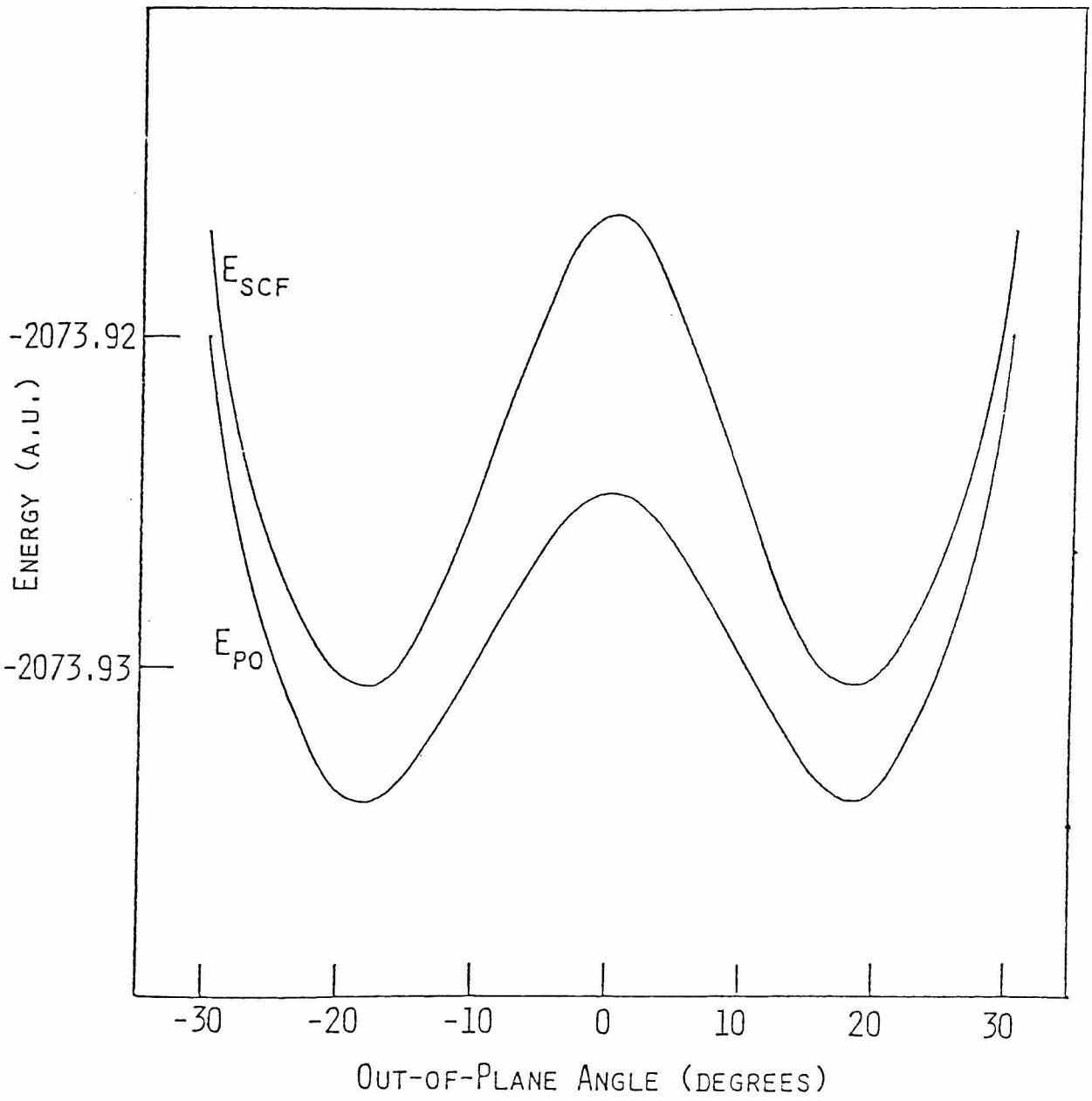

Figure 1(c). SCF (E_{SCF}) and pseudo-orbital (E_{PO}) energies for GeH_3 versus out-of-plane angle. Bond length is 1.554 Å.

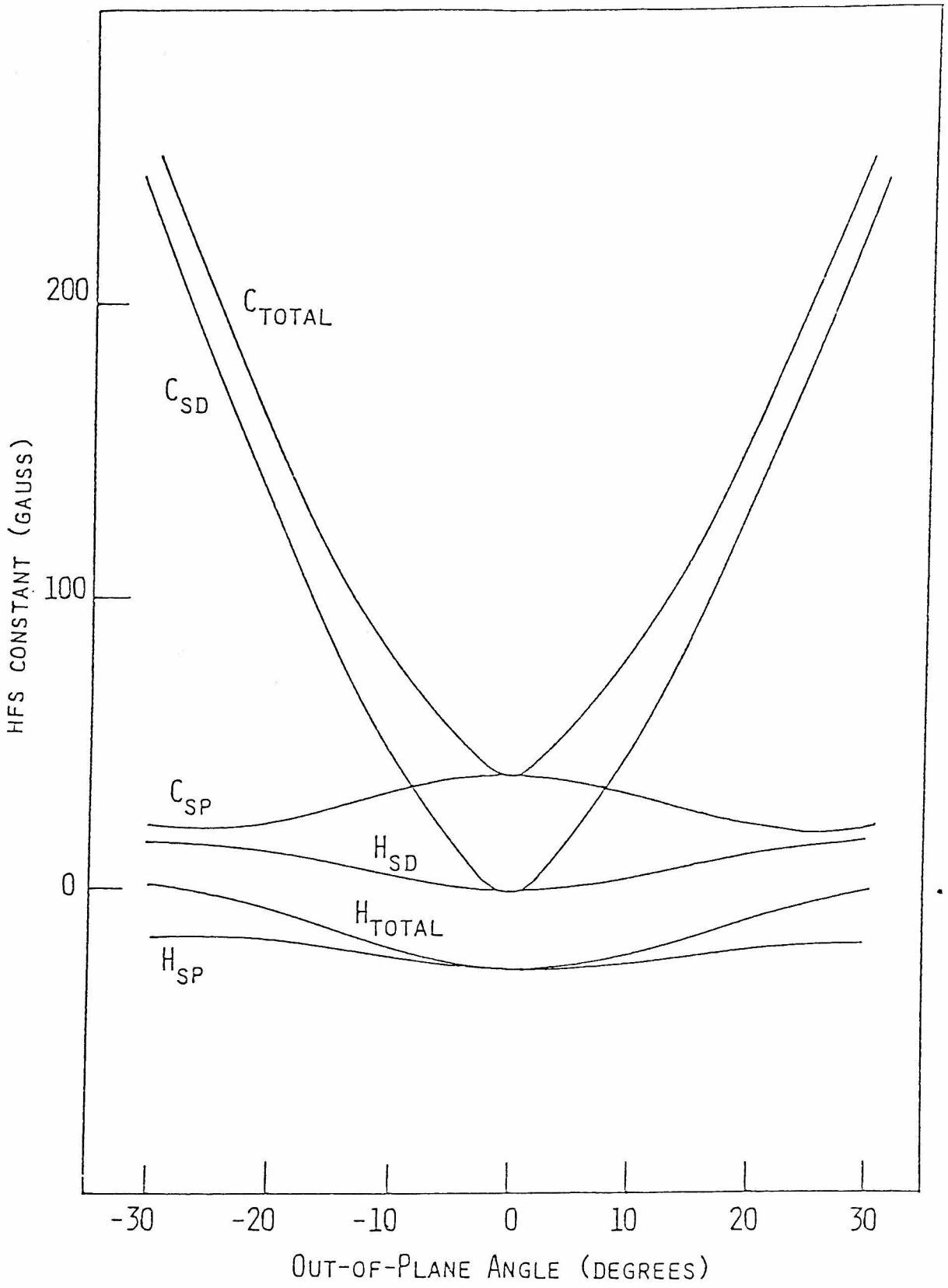

Figure 2(a). hfs constant for CH_3 versus out-of-plane angle. Equilibrium angle is 0° for CH_3.

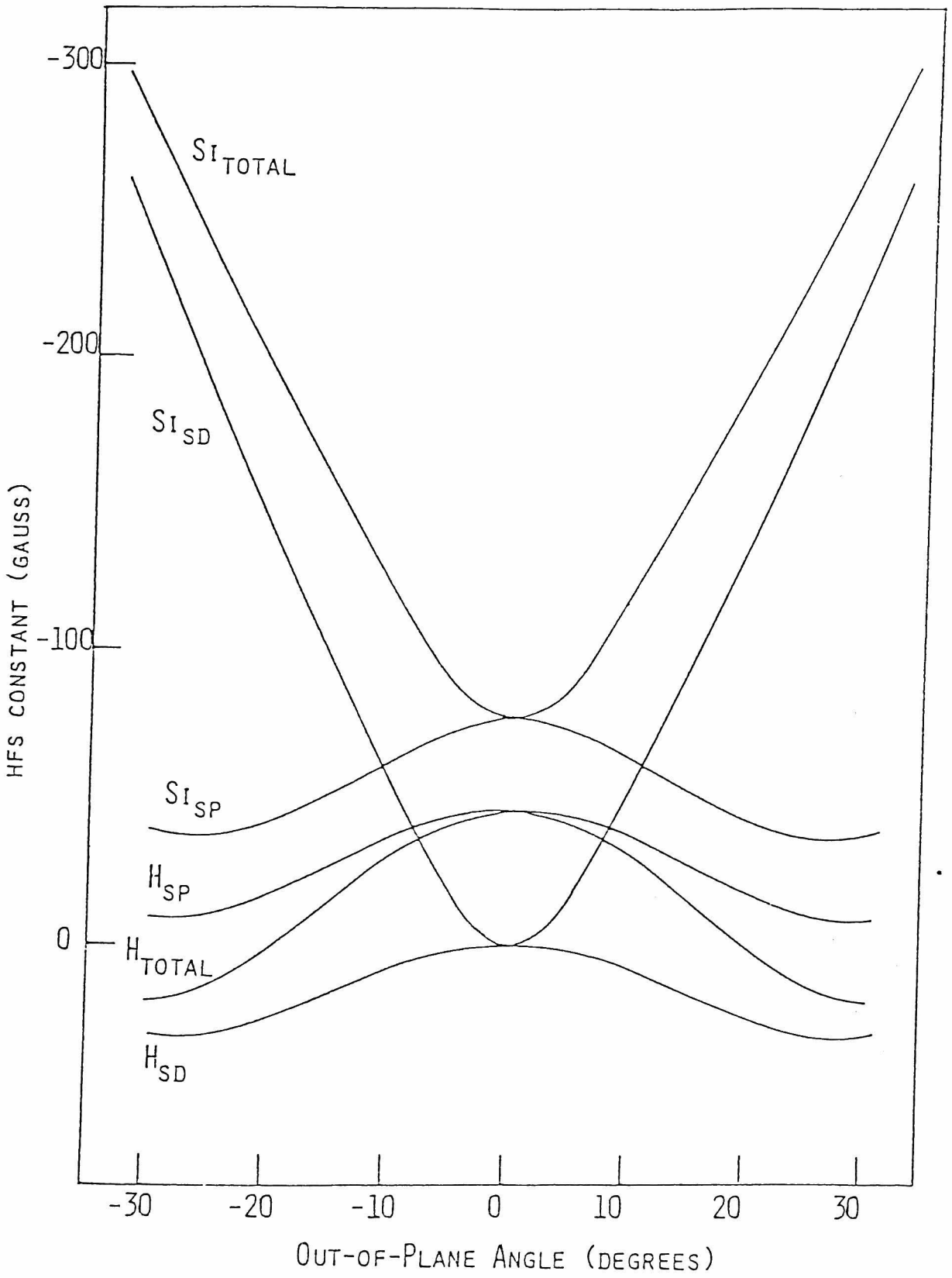

Figure 2(b). hfs constsnt for SiH_3 versus out-of-plane angle. Equilibrium angle is 16.1° for SiH_3.

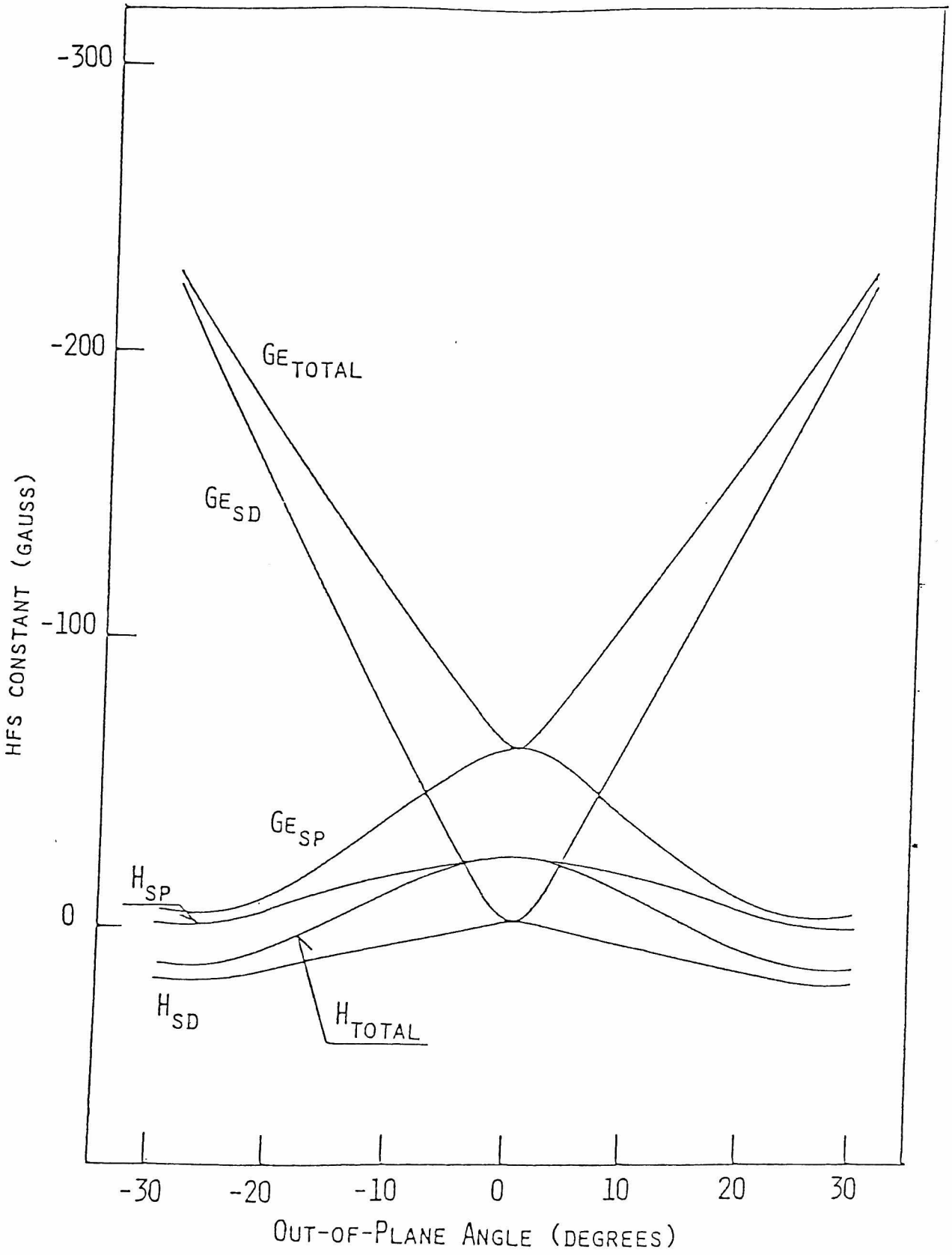

Figure 2(c). hfs constant for GeH_3 versus out-of-plane angle. Equilibrium angle is 18.4° for GeH_3.

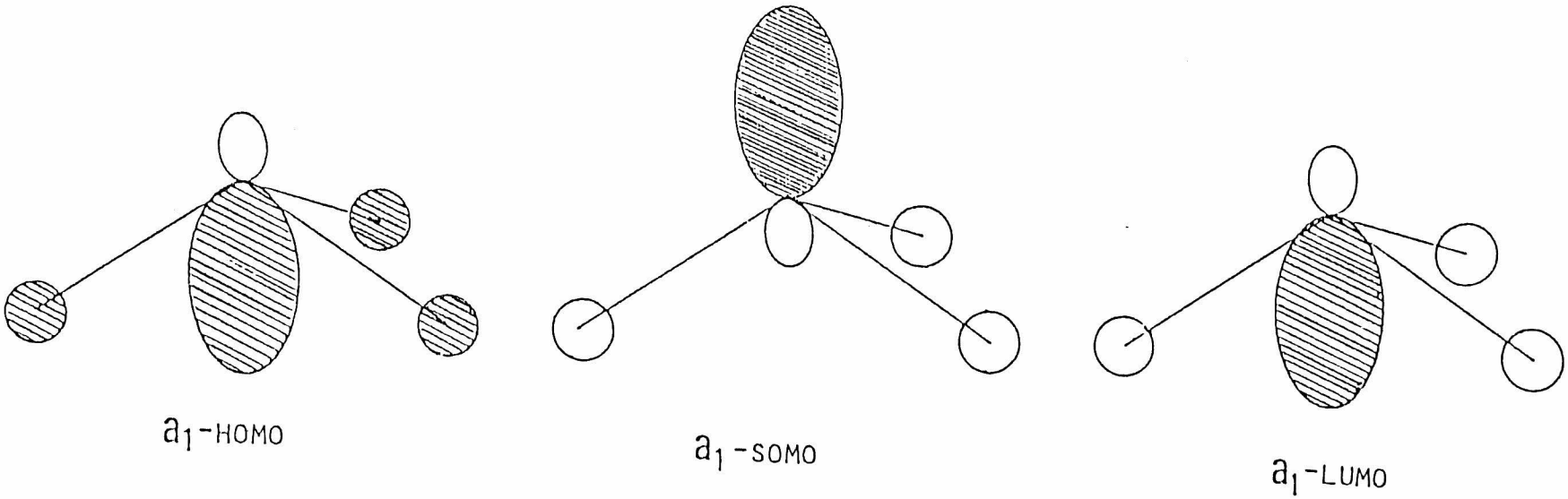

Figure 3. Schematic picture of three orbitals which make main contribution to spin-polarization effect.

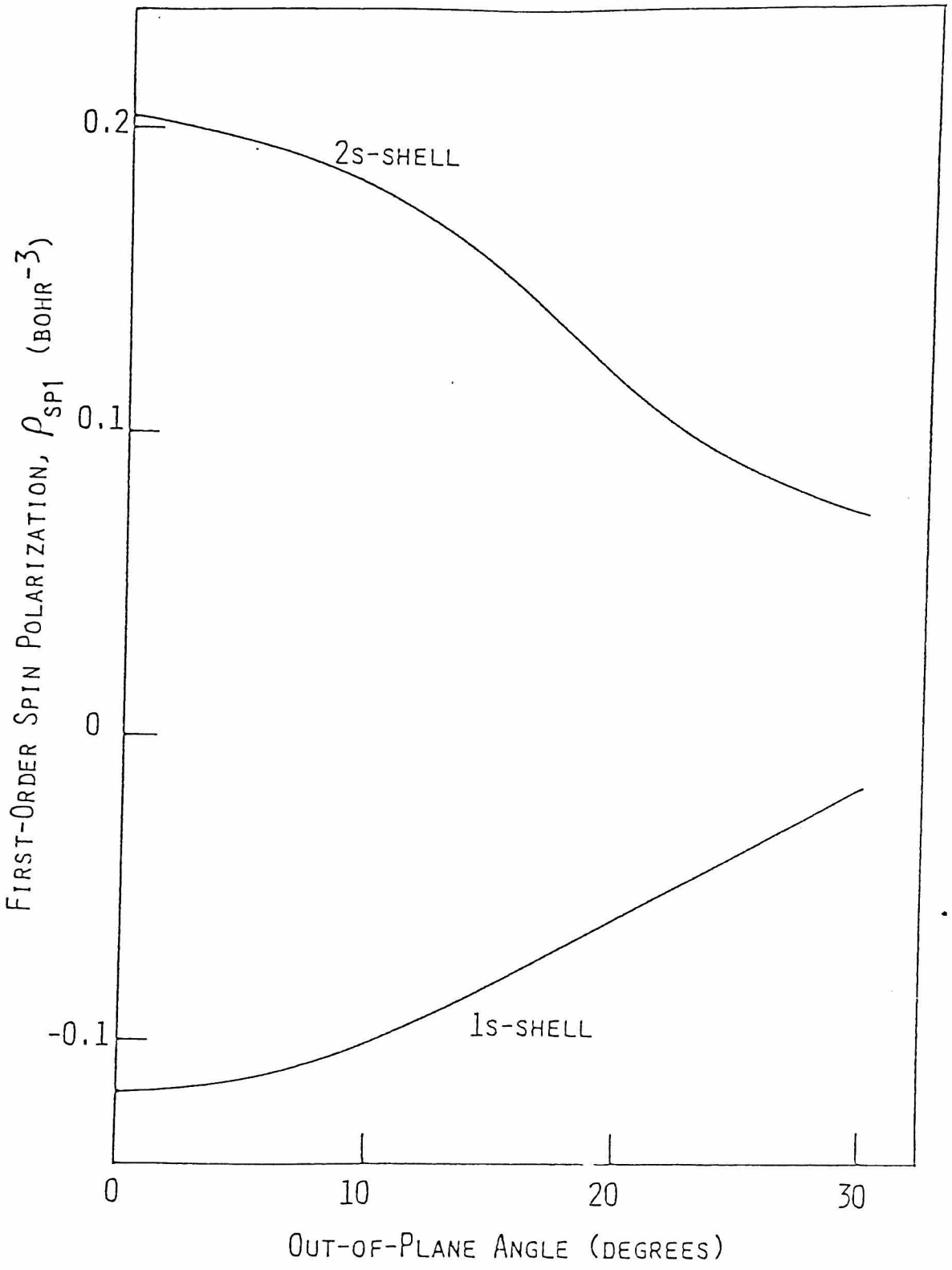

Figure 4(a). Shell analysis of the SP1 contribution for central nucleus C of CH_3.

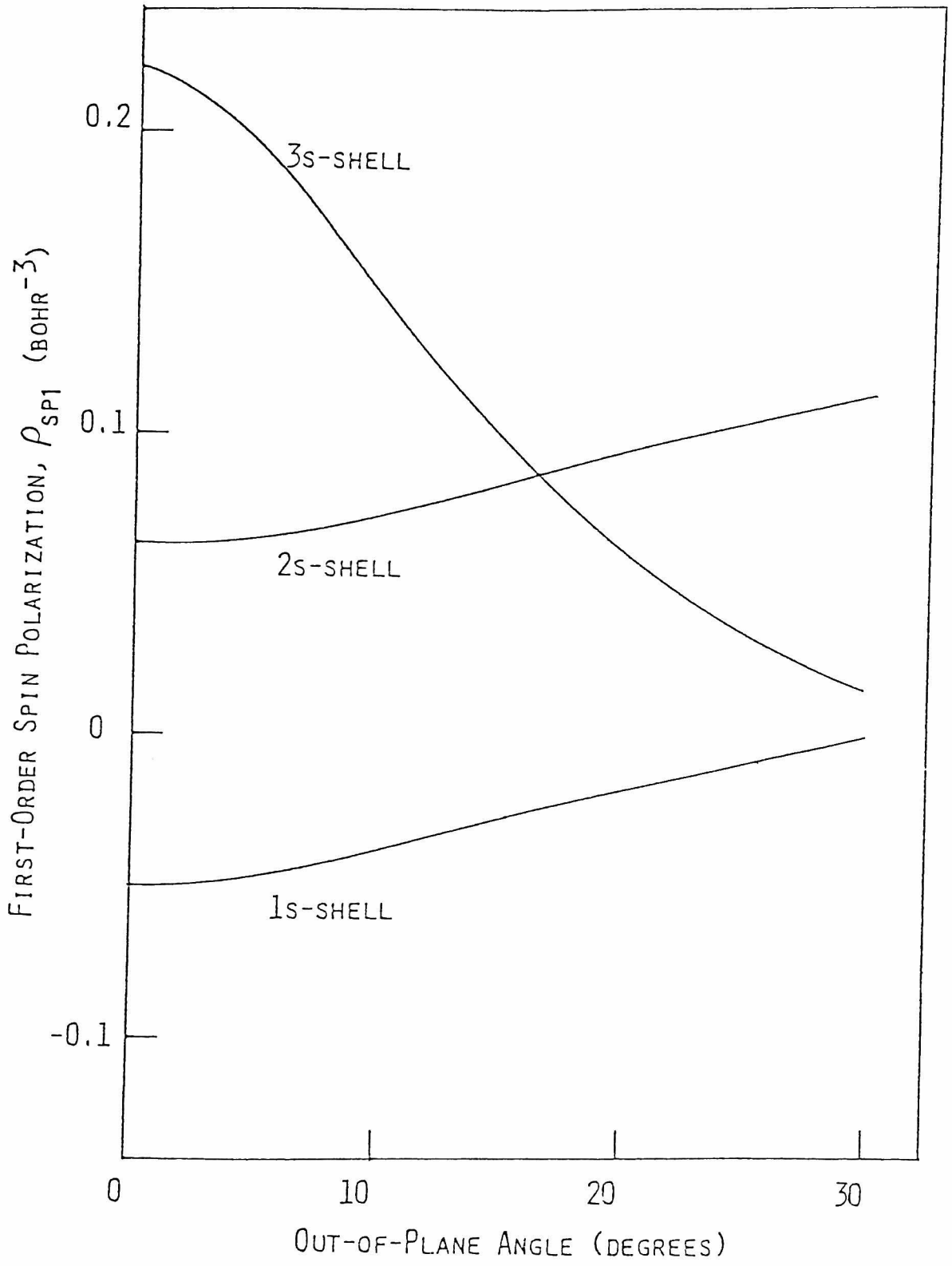

Figure 4(b). Shell analysis of the SP1 contribution for central nucleus Si of SiH_3.

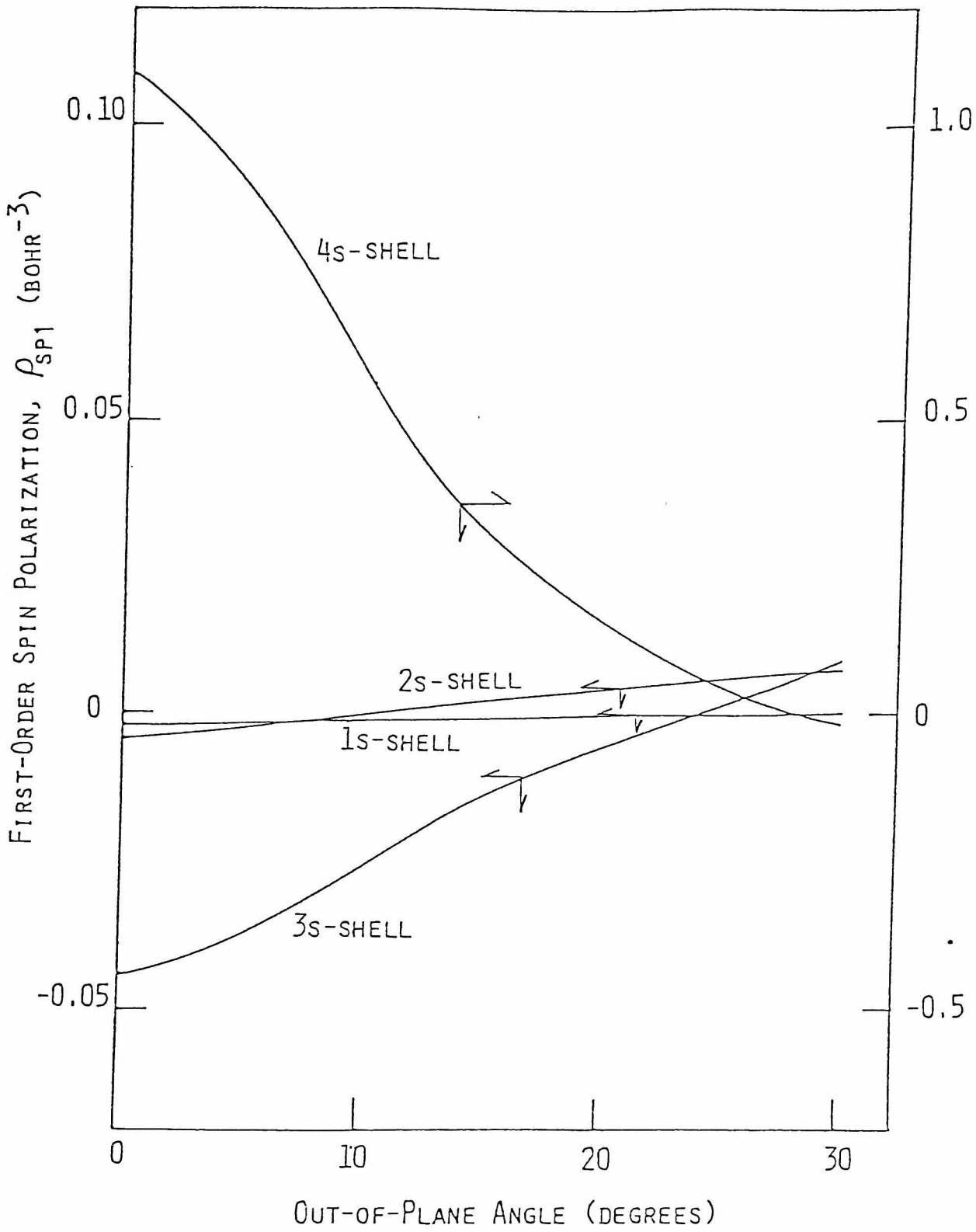

Figure 4(c). Shell analysis of the SP1 contribution for central nucleus Ge of GeH_3.

PART IV, Chapter 3

Jahn-Teller Effects for Molecular Structures and Spin Densities of Cation Radicals of Cyclopropane, Cyclobutane, and Cyclopentane

INTRODUCTION

For simple cycloalkanes Jahn-Teller (J-T) distortions are expected when an electron is removed from degenerate orbitals. The change in molecular geometry may be significant since an electron is removed from a valence σ orbital. In this study the molecular geometry of the cation radicals of cyclopropane, cyclobutane, and cyclopentane are calculated by an ab initio SCF-MO method for several low-lying electronic states to find the most stable state and its molecular geometry. The cation radicals of cyclopropane and cyclobutane in the ground electronic state are predicted to be distorted from D_{3h} to C_{2v} and from D_{2d} to D_2, respectively, in accordance with the J-T theorem. The distortion in the cation radical of cyclopentane from D_{5h} is found to be greater than the distortion in the neutral molecule which is well known to undergo pseudorotation between C_s and C_2 coformations[1].

In the next step the hyperfine splitting (hfs) constants are calculated by pseudo-orbital (PO) theory[2] for the optimized geometries to compare with observed ESR spectra of the cation radicals. It is inferred that the cation radical of cyclopropane undergoes facile dynamic J-T distortions at 77K whereas the cation radical of cyclopentane is subject to the dynamic J-T effect at about 100K because the observed hfs constants at these temperatures are in agreement with the average of the calculated hfs constants.

EXPERIMENTAL

Recently it is established that Υ-irradiated of frozen solutions in the CCl_3F matrix leads to an efficient production of cation radicals of solute molecules and their ESR spectrum can be measured without significant interference due to concomitantly produced paramagnetic species[3-6]. We applied this method to obtain ESR spectra of cation radicals of cyclopropane and cyclopentane[7]. Experimental procedures for irradiation and ESR measurements were described repeatedly elsewhere[3]. Cyclopropane and cyclopentane were commercially obtained and used as received. Cyclobutane was not studied because it was unobtainable. The ESR measurement was carried out at 77 to about 140K by using a JEOL FE spectrometer.

EXPERIMENTAL RESULTS

Figure 1 illustrates observed ESR spectra of Υ-irradiated solutions of cyclopropane in CCl_3F (@ 1 mol %) at 77K (Fig.1a) and cyclopentane in CCl_3F (@ 1 mol %) at 77K and at @100K (Fig.1b, 1c). Spectrum in Figure 1a did not change appreciably upon warming to @100K whereas the marked spectral change between Figure 1b and 1c was reversible. Upon further warming towards the melting point of CCl_3F (162K) part of the spectra changed irreversibly which indicates subsequent chemical reactions.

By analogy with the result of a number of aliphatic hydrocarbons in CCl_3F[3-6] the spectra in Figure 1 are assigned to the cation radicals of the respective cycloalkanes. The

reversible appearance of the eleven line spectrum on warming the cyclopentane solution strongly suggests that the ten protons of the cation radical become equivalent by ring puckering. Consequently, the complicated spectrum in Figure 1b is associated with the cation radical prior to the molecular motion.

Due to the poor resolution of Figure 1a it is not possible to obtain detailed information of the hyperfine structure for the cation radical of cyclopropane. However, a simulation assuming a set of six equivalent protons of a hfs constant of about 5G with a linewidth of 2G for each component reproduced fairly well the observed spectrum in Figure 1a. As will be discussed later, the cation radical in the lowest energy state is predicted to be distorted and the hfs constants be inequivalent. However, if the cation radical at 77K undergoes a dynamic distortion just as the cation radical of cyclopentane at @100K, the six protons will become equivalent in the time scale of ESR hyperfine interaction. Such an averaging has been known for the cation radical of benzene in rigid matrices at 77K [8-9].

THEORETICAL

Geometry optimization was performed by the energy gradient method with the HONDOG program[10], where an unrestricted HF (UHF) wavefunction with the STO-4G minimal basis set[11] was employed. Hfs constants were calculated for the optimized geometries by applying the PO (pseudo-orbital) theory with an RHF wavefunction

as reference wavefunction. We emphasize that we did not use the UHF wavefunction for the calculation of hfs constants. The UHF wavefunction does not satisfy spin-symmetry and its inadequacy for the calculation of spin correlation is well known[12]. On the other hand, the PO theory, which includes spin-polarized single excitations in a framework of the symmetry-adapted-cluster (SAC) expansion theory[13], satisfies pure spin-symmetry and takes a proper account of the spin correlation effect. It has been applied to various organic and inorganic radicals and fairly good results have been obtained[2]. Calculated hfs constants were analyzed by partitioning to spin-delocalization (SD) and spin-polarization (SP) contributions[14]. The SD contribution comes from the delocalization of unpaired electron in the singly occupied orbital and is therefore always non-negative. On the other hand, the SP contribution comes from the spin correlation and becomes both positive and negative. The total hfs constant is the sum of these two contributions.

It is also important to select the basis set carefully in the calculation of hfs constants because the basis set dependence of the calculated result is not so small. In the previous work[2c], we used double ζ CGTO basis set which is contracted to be suited for the calculation of hfs constants[15] and obtained fairly good results. Here, the hfs constants of cyclopropane cation radical were calculated with the double ζ basis set and with the STO-4G minimal basis set for the geometry optimized with the latter basis set. In the Appendix we showed the difference in the calculated hfs constants: the difference is relatively small (~3G) for the protons but very large for the

carbons. For the cation radical of cyclopropane, the result of double ζ basis set should be more reliable[2c]. For cyclobutane and cyclopentane cations, the hfs constants are calculated with only the STO-4G basis, therefore the discussion for the latter cations is limited to the proton hfs constants.

COMPUTATIONAL RESULTS AND DISCUSSION

Cyclopropane

We first calculated the MO of neutral molecule for an experimentally determined geometry of D_{3h} (r(CC)=1.524Å, r(CH)=1.07Å, ∠HCH=120°)[16] by a standard STO-4G basis. As shown in Figure 2, the orbital symmetry of HOMO is e'(σ) and the nature of the orbital is in-plane σ bonding along the carbon frame. The orbital next to HOMO (NHOMO) has e"(π) symmetry and the character is of σ bonding for the C-H bonds and of π bonding for the C-C bonds. The σ bonding character is stronger than the π bonding. According to the J-T theory, the molecular geometry will be distorted from D_{3h} to C_{2v} by removing an electron from one of these degenerate orbitals. Figure 3 shows the state correlation diagram. The J-T distortion associated with the e'(σ) orbital generates $^2A_1$ and $^2B_2$ states of a C_{2v} conformation. On the other hand, the J-T distortion associated with NHOMO e"(π) orbital yields $^2A_2$ and $^2B_1$ states. Thus, four distinct electronic states are generated. Geometry optimization was performed for all of the four states of C_{2v} symmetry.

Figure 4 shows the state level diagram obtained for the fully optimized geometries. Figure 5 shows the nodal pattern of the singly occupied orbital, the geometry optimized with the STO-4G basis, and the hfs constants calculated by the double ζ basis set (the values in parentheses show the SD and SP contributions). Figure 5a, 5b, 5c, and 5d are for the $^2A_1$, $^2B_2$, $^2B_1$, and $^2A_2$ states respectively.

The J-T distortion in these doublet states can be understood with reference to the nodal pattern of the singly occupied orbital; when an electron is removed from an orbital of anti-bonding nature, the bond will be shortened whereas the removal from a bonding orbital will cause the bond elongation. Accordingly, in the $^2A_1$ state a stable geometry will be a flattened triangle II in figure 3 because the singly occupied orbital of a_1 symmetry is anti-bonding between C_1 and C_2 and bonding between C_2 and C_3. In the $^2B_2$ state the singly occupied orbital is anti-bonding between C_2 and C_3 and bonding between C_1 and C_2 and between C_1 and C_3. A stable geometry will therefore be a vertically elongated triangle I in Figure 3. Similarly, the stable geometries for the $^2A_2$ and $^2B_1$ states originating from the e"(R_x,R_y) orbitals are predicted as shown in Figure 3. In these states the change in the C-H length should be larger than that in the C-C length because the e" orbitals are the C-H σ bonding orbitals. The above qualitative predictions are, in fact, born out by the ab initio calculations as described below.

The two lowest states of cyclopropane cation radical are calculated to be very close in energy as shown in Figure 4. The energy difference between the first two states $^2A_1$ and $^2B_2$

calculated by the open-shell RHF method with the double ζ basis set (the UHF method with the STO-4G basis set) is only 3.5 (4.9) kcal/mol and that of the upper two states $^2B_1$ and $^2A_2$ is 13.5 (13.4) kcal/mol. The difference between the average of $^2A_1$ and $^2B_2$ and the average of $^2B_1$ and $^2A_2$ is 68.0 (82.8) kcal/mol. From the orbital energies shown in Figure 2 and the Koopmans' theorem, the energy difference between the cationic states obtainable from the vertical ionization from the orbitals e'(σ) and e"(π) is expected to be 3.3eV (= 75 kcal/mol).

$^2A_1$ State

The nodal picture of singly occupied orbital, the optimized geometry, and hfs constant are shown in Figure 5a. The C_2-C_3 bond is elongated by as much as 0.32Å and the C_1-C_2 and C_1-C_3 bonds are shortened by 0.02Å relative to the neutral molecule. The HCH angles are 116.5° and 118.0° at C_1 and at C_2 and C_3 respectively (cf. ∠HCH=120° in the neutral molecule). The total hfs constants are given with the components of SD and SP in parentheses. At the C_1 site, the carbon hfs constant is negative, -13.2G, and the proton hfs is positive, 16.5G. On the other hand, at C_2 or C_3 site, the carbon hfs value is positive, 18.3G and that of proton hfs is negative, -12.3G. The averaged hfs constants are then relatively small, 7.8G and -2.7G for carbon and proton, respectively.

$^2B_2$ State

The C_2-C_3 bond is shortened by 0.1Å and the other two elongated by 0.16Å as shown in Figure 5b. The change in angle

of HCH is relatively small. The local electronic structure at C_1 is similar to that of the methyl radical and the proton hfs constant of -19.9G comprises solely the SP contribution. The hfs constant of C_1 is also determined solely by the positive SP contribution 14.1G.

$^2B_1$ State

The relatively large change in the C_1-H_4 and C_1-H_7 by 0.11Å is reasonable because the singly occupied orbital has a σ bonding nature in the C-H bond region. The small angle of HC_1H makes the overlap of p-orbital of C_1 perpendicular to the molecular plane with the s-orbitals of H_4 and H_7 large. This leads to a SD contribution as large as 175G and the total hfs constant amounts to 203G at these protons. The experimental test of the predicted large hfs constant in this excited state may be interesting. For the carbon ring, the singly occupied orbital has a π nature and all of the carbon hfs constants comprised only the negative SP contributions.

$^2A_2$ State

The small angles of HC_2H and HC_3H of 97.2° in Figure 5d are notable. As a result, a large hfs constant, 141G, is predicted for the protons attached to C_2 and C_3. The largest carbon hfs value is -21.6G at the bottom of the elongated triangle.

From the above result the cation radical of cyclopropane

in the ground state is concluded to be the $^2A_1(\sigma)$ state. The proton hyperfine structure should be characterized by the constants of -12.3 and 16.5G (cf. Fig.5a) if the distortion is static. The observed spectrum is, however, much smaller hfs constant of about 5G as stated before. The apparent discrepancy may be removed if we consider that the dynamic J-T distortions within $^2A_1$ state and/or between $^2A_1$ and $^2B_2$ states take place at 77K. The energy difference between the near degenerate $^2A_1$ and $^2B_2$ is calculated as only 3.5 kcal/mol and the averaged proton hfs constants are -2.7 and -1.9G, respectively. The observed hfs constant of about 5G may be compared with the average of the two. In this connection experiments at lower temperatures should be interesting.

Cyclobutane

Figure 6 shows the orbital energy levels of the neutral molecule of cyclobutane calculated for an experimentally determined geometry of D_{2d} symmetry (r(CC)=1.555Å, r(CH)=1.087Å, CCC=87.2°, and ∠HCH=108.6°)[17]. HOMO's are degenerate with a σ nature in the carbon frame. Another set of e orbitals are at -13.9eV. They are of a π nature in the carbon frame and of a σ nature in the CH bonds. The cation radicals generated from these sets of e orbitals will be distorted from D_{2d} to C_{2v} or D_2 by the J-T effect as shown in Figure 7. After geometry optimization, the most stable state is calculated to be $^2B_3$ of D_2 symmetry, and the next lowest state to be $^2B_2$ of C_{2v}

symmetry. However, the most stable state is $^2B_3$ of D_2, these two states differ in energy only by 1.1 kcal/mol and therefore are almost degenerate.

In the normal mode connecting D_{2d} and D_2 geometries, the C_1-C_3 length is elongated and the C_1-C_2 length is shortened as shown in Figure 7. Then, in the D_2 symmetry, the cation of $^2B_3$ symmetry is more stable than the $^2B_2$ cation, since in the former the singly occupied orbital is bonding between C_1 and C_3 and anti-bonding between C_1 and C_2 as shown in the top of Figure 8a. In the normal mode connecting D_{2d} and C_{2v} geometries, the C_1-C_4 length is elongated and the C_2-C_3 length is shortened. Therefore the $^2B_2$ state in which the SOMO is bonding between C_1 and C_4 and anti-bonding between C_2 and C_3 is more stable than the counterpart $^2B_1$ state. Since the key interaction in the latter deformation is between non-bonding carbons, i. e., C_1-C_4 and C_2-C_3, the stablization obtained by the Jahn-Teller distortion should be smaller than in the deformation from D_{2d} to D_2 geometry. The result of the ab initio calculation is parallel to this interpretation. The calculated energy difference is, however, as small as 1.1kcal/mol. This is interpreted as due to a mixing between states of the same symmetry. In the D_2 symmetry, the $^2B_3$ state originating from the $E(R_x,R_y)$ state is higher in energy than the $^2B_2$ state, whereas in the C_{2v} symmetry the $^2B_2$ state originating from the $E(R_x,R_y)$ state is lower than the $^2B_1$ state (see Figure 7). Therefore, the stabilization of the ground state due to a mixing with higher state with the same symmetry is more advantageous for the C_{2v} distortion than for the D_2 distortion. Though this

effect seems to be secondary, it works to diminish the energy difference between $^2B_3$ in D_2 and $^2B_2$ in C_{2v}.

$^2B_3$ State in D_2

The singly occupied orbital, the optimized geometry, and the hfs constants are given in Figure 8a. The bond between C_1 and C_3 is elongated by 0.16Å and that of C_1 and C_2 is shortened by 0.07Å relative to the neutral molecule. The hfs constant of the equatorial protons is calculated as 25.4G which comprises the SD contribution of 23.8G. This is due to a large overlap between the equatorial protons and the σ lobes of the singly occupied orbital as shown in Figure 8a.

$^2B_2$ State in C_{2v}

The distance between C_1 and C_4 is lengthened by 0.242Å and that of C_2 and C_3 shortened by 0.143Å from 2.145Å of the neutral D_{2d} geometry. These changes are very large partly because these pairs are non-bonding, and are consistent with the nodal pattern of the singly occupied orbital. The hfs constant of the equatorial protons is as large as 81.8G owing to a large overlap with the radical lobes.

The energy differences between these two states is only 1.1 kcal/mol. Thus, the proton hfs constants will be averaged and eight equivalent protons will give a nine spectrum of the average constant of 15.4G unless the experiment is carried out at very low temperatures. The average proton hfs constant of the $^2B_3$ (D_2) state is 12.2G and that of $^2B_2$ (C_{2v}) is 18.5G.

Cyclopentane

The neutral molecule is known to undergo pseudorotation between C_s and C_2 conformations[1]. The cation radical is also considered to be distorted to C_s and C_2. In the present work the ab initio calculations were made only for the C_s structure. The singly occupied orbital, the optimized geometry, and the hfs constants are given in Figure 9. In consistence with the singly occupied orbital the C_1-C_2 and C_1-C_3 bonds are lengthened by 0.14Å from the neutral molecule[17]. The $C_2C_3C_4C_5$ frame is little distorted from D_{5h}. A large hfs constant of 43.4G is calculated for the equatorial protons of H_7 and H_8. The constants of H_6 and H_{11} are negative being contributed solely by SP. The average of hfs constants becomes 4.3G which is slightly smaller than the observed constant of 7.7G in the spectrum of Figure 1c.

CONCLUSION

In this work geometry optimization was carried out for several electronic states of cation radicals of cycloalkanes. The calculated distortions relative to the neutral molecules are consistent with the nodal picture of singly occupied orbitals. Hfs constants calculated by the PO theory reflect the distortion of geometry sensitively through a large spin-delocalization. The calculated hfs constants agree well with the experimental

results of cation radicals of cyclopropane and cyclopentane if the dynamic J-T distortion is assumed for near-degenerate electronic states.

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Appendix

The hfs constants obtained by the double ζ and STO-4G minimal basis sets are compared in Table.1 for the $^2A_1$ ground state of cyclopropane cation radical. The largest change in the calculated values is 21.2G at the hfs constant of C_2 which is the bottom of the flattened triangle as shown in Fig. 5a. Especially the SP contribution changed by as large as 31.1G. The carbon hfs constant at the top of the triangle and the proton hfs constants have not changed so largely. In Table.2 we show the differences in the averaged hfs constants for each of the four states of cyclopropane cation. The carbon hfs constants in the $^2A_1$ and $^2B_2$ states have changed largely. The change in the proton hfs constant is about 3G ~ 4G. For the upper two states, $^2B_1$ and $^2A_2$, the hfs constants increased for both of the proton and carbon in the calculation with STO-4G minimal basis set. In the $^2B_1$ state, the difference in the averaged proton hfs value is rather large, i. e., 8.4G. This comes from the large values at H_4 and H_7 in Fig. 5c which is 203G and 230G by the double ζ and the STO-4G minimal basis sets, respectively.

References

(1) (a) D. Cremer and J. A. Pople, J. Am. Chem. Soc., 97, 1358 (1975). (b) E. Diez, A. L. Esteban, F. J. Bermejo, and M. Rico, J. Phys. Chem., 84, 3191 (1980).

(2) (a) H. Nakatsuji and K. Hirao, Chem. Phys. Lett., 47, 569 (1977). (b) H. Nakatsuji and K. Hirao, J. Chem. Phys., 68, 4279 (1978). (c) K. Ohta, H. Nakatsuji, K. Hirao and T. Yonezawa, J. Chem. Phys., 73, 1770 (1980).

(3) (a) T. Shida and T. Kato, Chem. Phys. Lett., 68, 106 (1979). (b) T. Shida, Y. Egawa, and H. Kubodera, J. Chem. Phys., 73, 5963 (1980). (c) T. Shida, H. Kubodera, and Y. Egawa, Chem. Phys. Lett., 79, 179 (1981). (d) H. Kubodera, T. Shida, and K. Shimokoshi, J. Phys. Chem., 85, 2583 (1981).

(4) (a)K. Toriyama, K. Nunome, and M. Iwasaki, J. Chem. Phys., 85, 2149 (1981). (b) M. Iwasaki, K. Toriyama, and K. Nunome, J. Am. Chem. Soc., 103, 3591 (1981).

(5) M. C. R. Symons and I. G. Smith, J. Chem. Research (S), 382 (1979).

(6) J. T. Wang and F. Williams, J. Phys. Chem., 84, 3156 (1980).

(7) A preliminary report was presented at the 24-th Symposium of Radiation Chemistry, Kyoto, October 1980.

(8) M. K. Carter and G. Vincow, J. Chem. Phys., 47, 292 (1967).

(9) O. Edlund, P. -O. Kinell, A. Lund, and A. Shimizu, J. Chem. Phys., 46, 3679 (1967).

(10) (a) H. F. King, M. Dupuis, and J. Rys, Program Library HONDOG (No.343) of Computer Center of the Institute for Molecular Science, 1979. See also, M. Dupuis, J. Rys, and H. F. King, QCPE, No.338 (1977). (b) M. Dupuis, J. Rys,

and H. F. King, J. Chem. Phys., 65, 111 (1976). (c) M. Dupuis and H. F. King, J. Chem. Phys., 68, 3998 (1978).
(11) W. J. Hehre, R. F. Stewart, and J. A. Pople, J. Chem. Phys., 51, 2657 (1969).
(12) H. Nakatsuji, J. Chem. Phys., 59, 2586 (1973).
(13) H. Nakatsuji and K. Hirao, J. Chem. Phys., 68, 2053 (1978).
(14) H. Nakatsuji, H. Kato, and T. Yonezawa, J. Chem. Phys., 51, 3175 (1969).
(15) Y. Ellinger, A. Rassat, R. Subra, and G. Berthier, J. Chem. Phys., 62, 1 (1975).
(16) Landolt-Bornstein, New Series, Vol.II/7 "Structure Data of Free Polyatomic Molecules" K. -H. Hellwege and A. M. Hellwege Ed., Springer-Verlag Berlin (1976).
(17) "Tables of Interatomic Distances and Configuration in Molecules and Ions", L. E. Sutton Ed., The Chemical Society, London (1958, 1965).

Table.1 hfs constants of cyclopropane cation radical in $^2A_1$ (gauss)[a].

Nucleus[b]		Double ζ	STO-4G
	SD	0.5	1.5
C_1	SP	-13.8	-16.6
	TOTAL	-13.2	-15.1
	SD	12.5	2.6
C_2	SP	5.8	36.9
	TOTAL	18.3	39.5
	SD	6.4	10.9
H_4	SP	10.1	6.9
	TOTAL	16.5	17.9
	SD	1.3	1.3
H_5	SP	-13.6	-19.4
	TOTAL	-12.8	-18.1

a: Result of the PO theory.

b: See Fig.5a for the position of the nucleus.

Table.2 Averaged hfs constants of cyclopropane cation (gauss)[a].

State	Nucleus	Double ζ	STO-4G	Difference
$^2A_1$	C	7.8	21.3	13.5
	H	-2.7	-6.1	-3.4
$^2B_2$	C	2.1	18.9	16.8
	H	-1.9	-5.7	-3.8
$^2B_1$	C	-10.4	-4.3	6.1
	H	79.3	87.7	8.4
$^2A_2$	C	-15.6	-11.3	4.3
	H	93.0	96.3	3.3

a: Result of the PO theory.

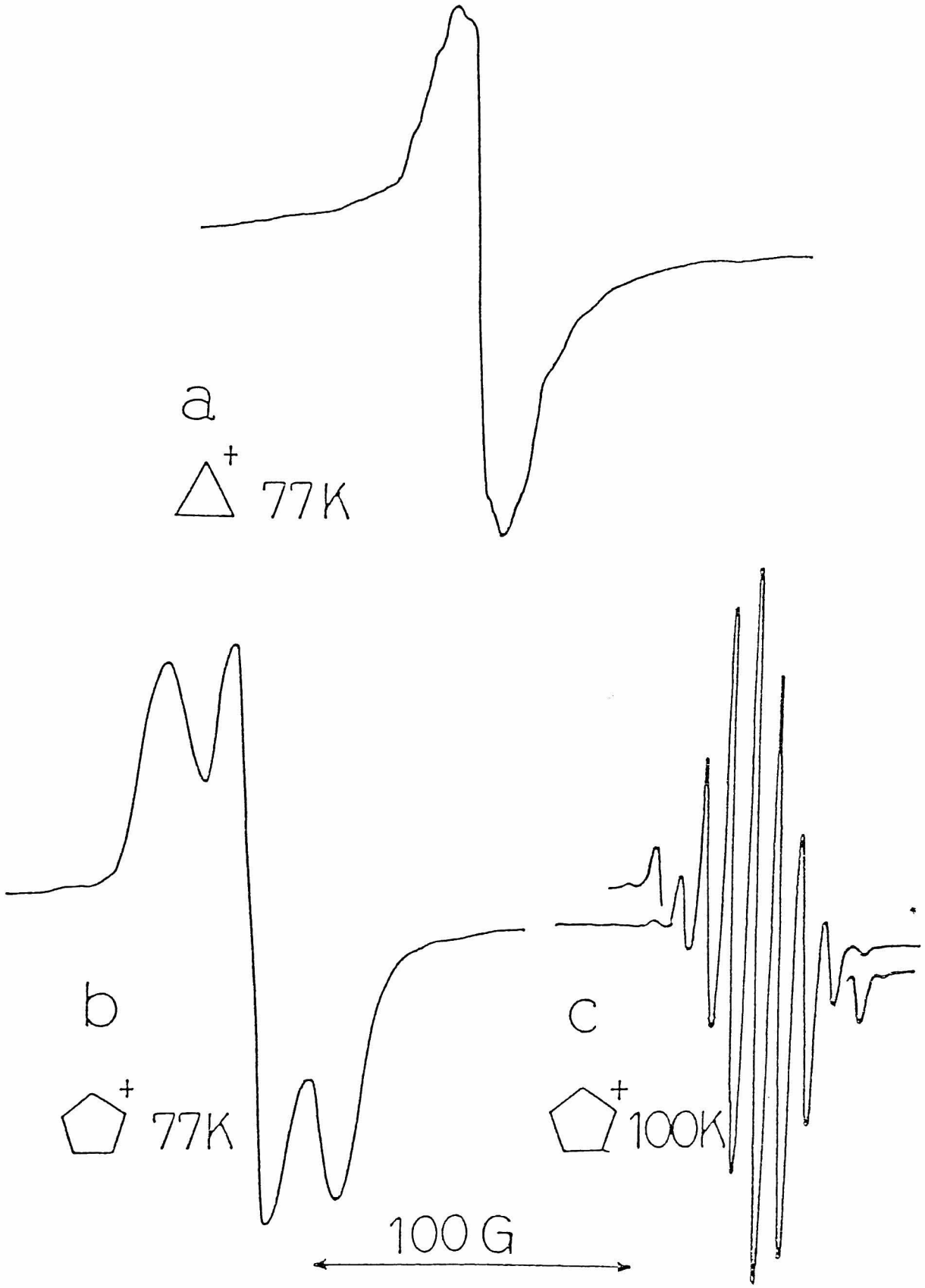

Figure 1. Observed ESR spectra of cation radicals of cycloalkanes in CCl_3F at 77K. a) cyclopropane at 77K, b), c) cyclopentane at 77 and 100K. Spectra in b) and c) change reversibly.

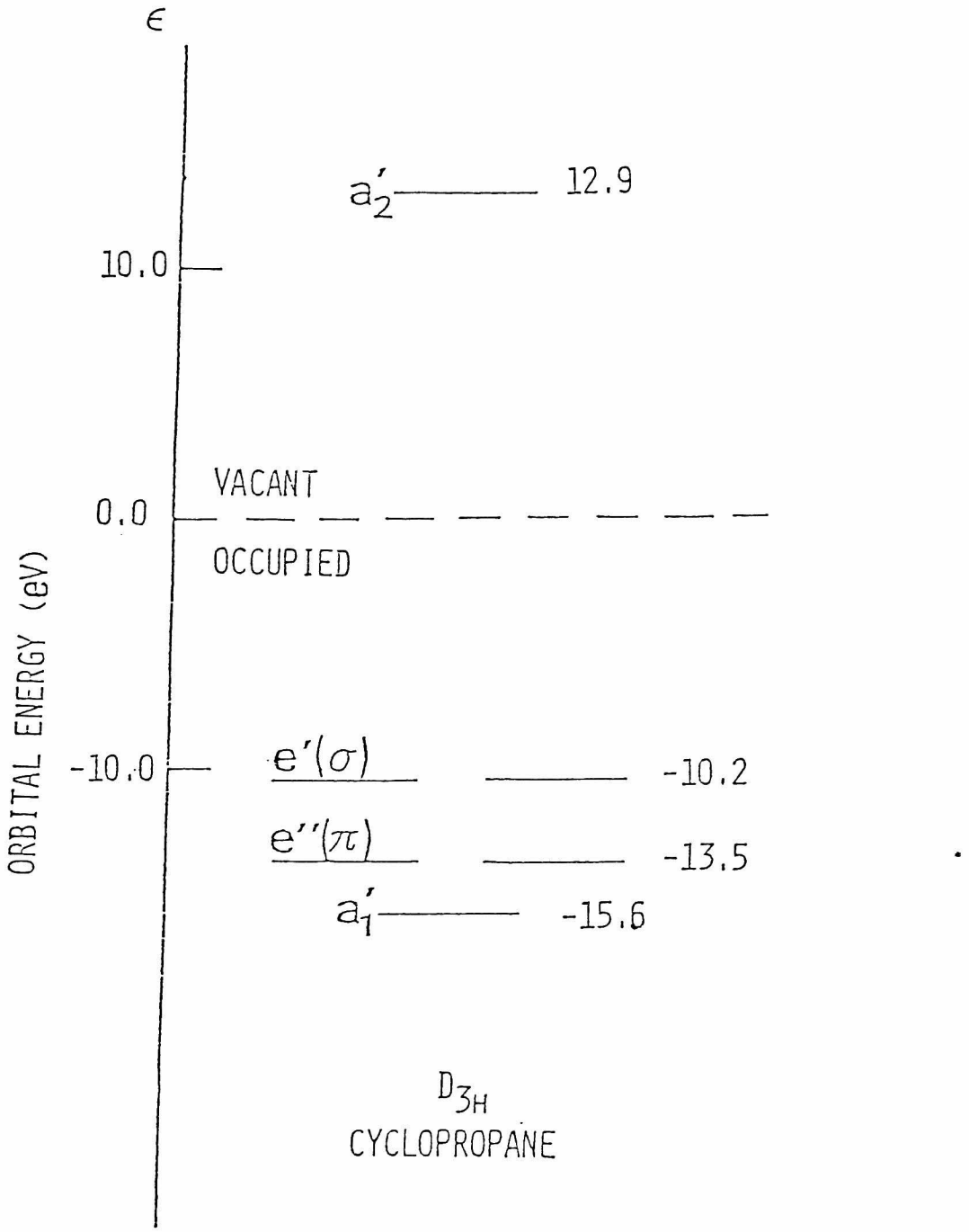

Figure 2. Orbital energy levels of neutral molecule of cyclopropane.

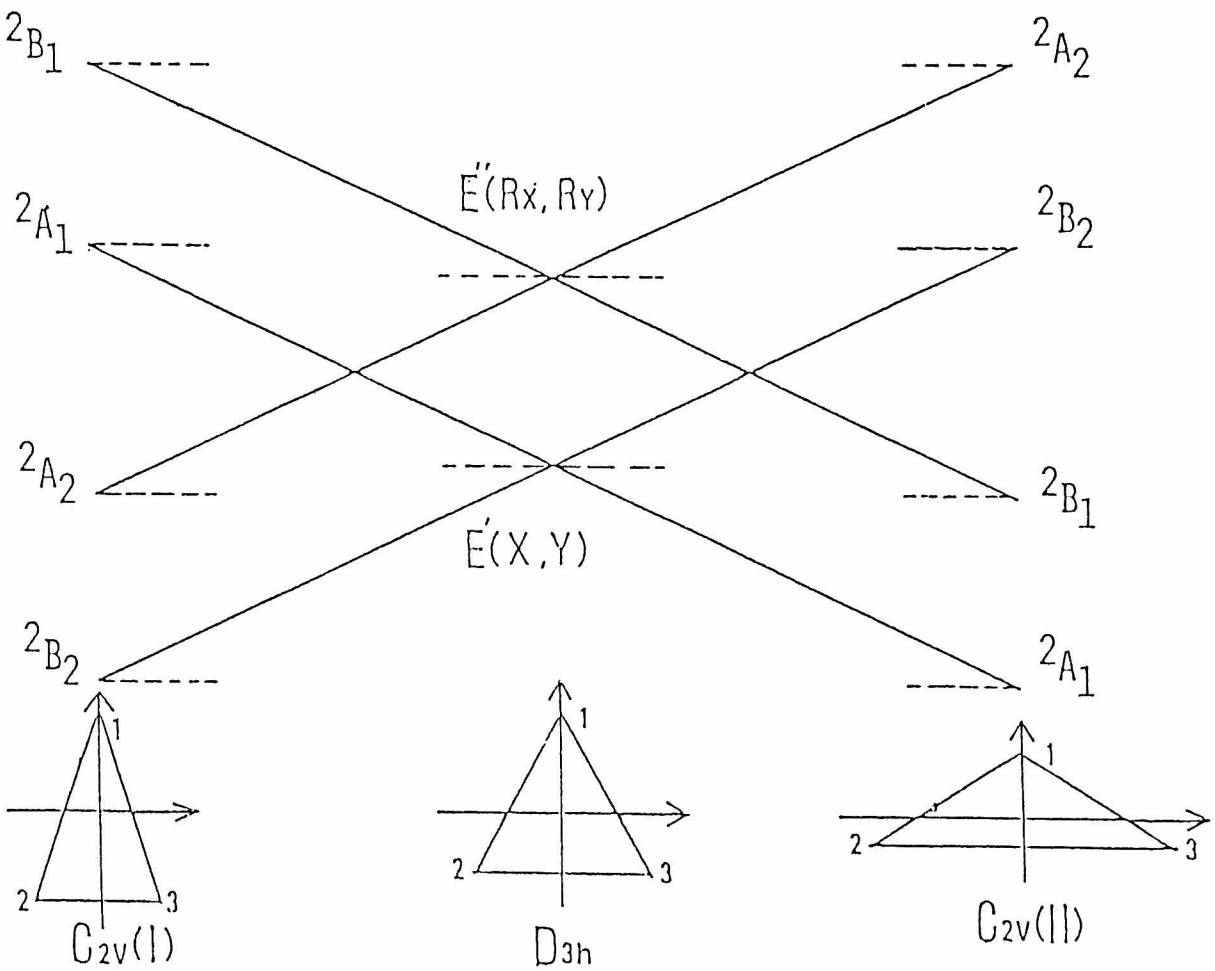

Figure 3. Correlation diagram of cation radical of cyclopropane.

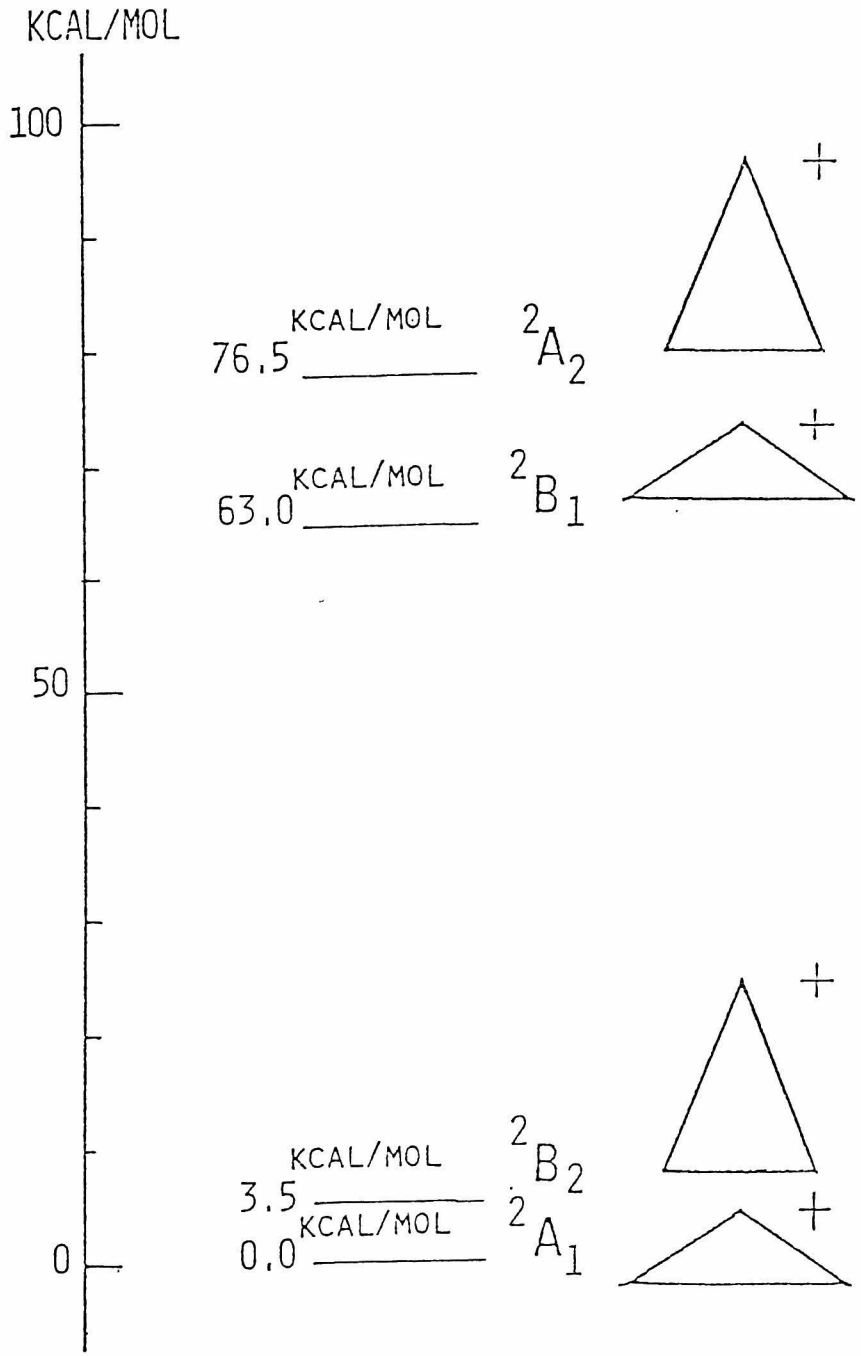

Figure 4. State level diagram of cation radical of cyclopropane. Result of the open-shell RHF wavefunction with the double ζ basis set.

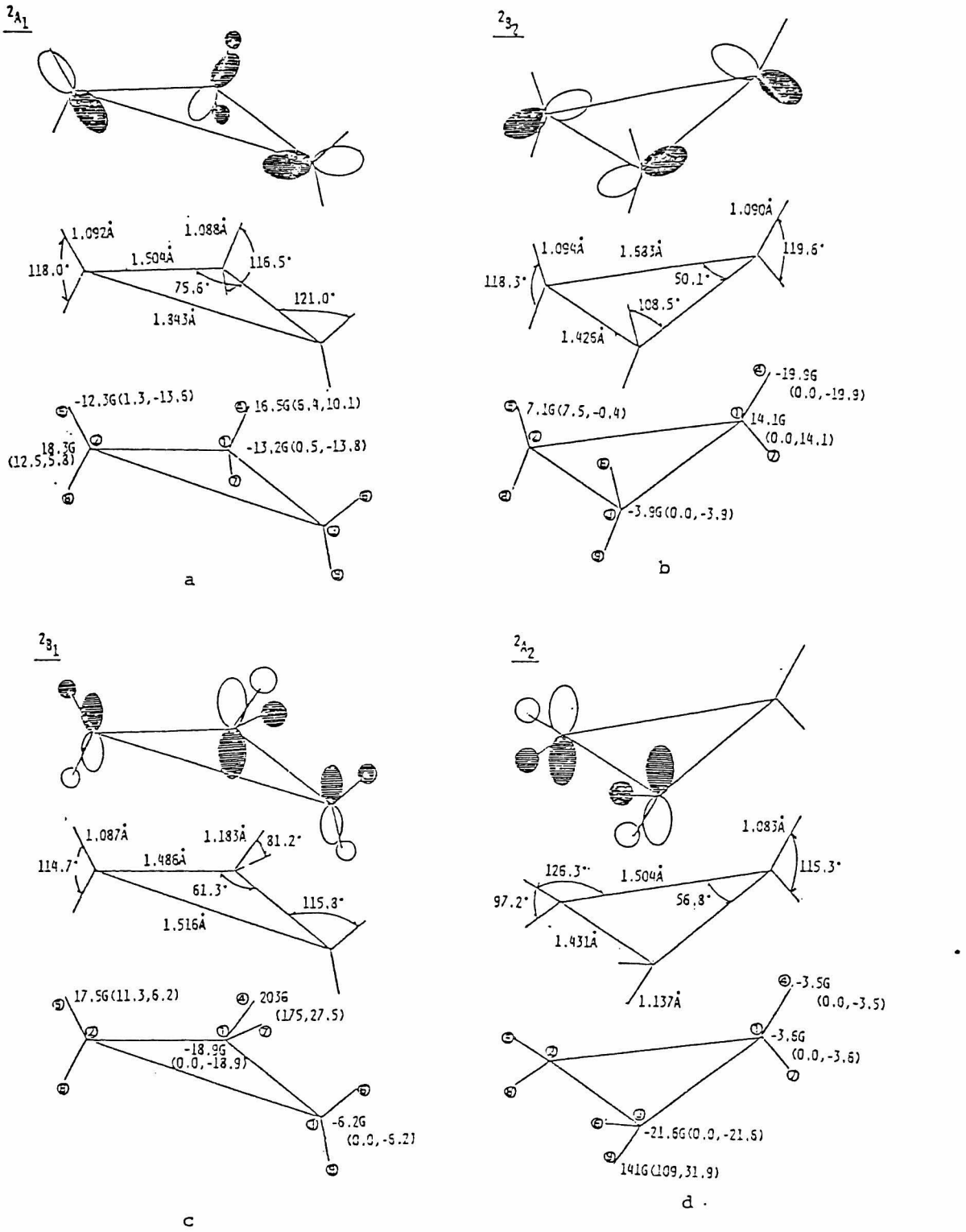

Figure 5. Nodal pattern of singly occupied orbital in the optimized geometry and hfs constants of cyclopropane cation radical. Hfs constants are calculated by the PO theory with the double ζ basis set. Experimental geometry of the neutral D_{3h} molecule is CC = 1.524Å, CH = 1.07Å, ∠HCH = 120°. SD and SP contributions of hfs constants are given in the parentheses as (SD, SP) in gauss unit.

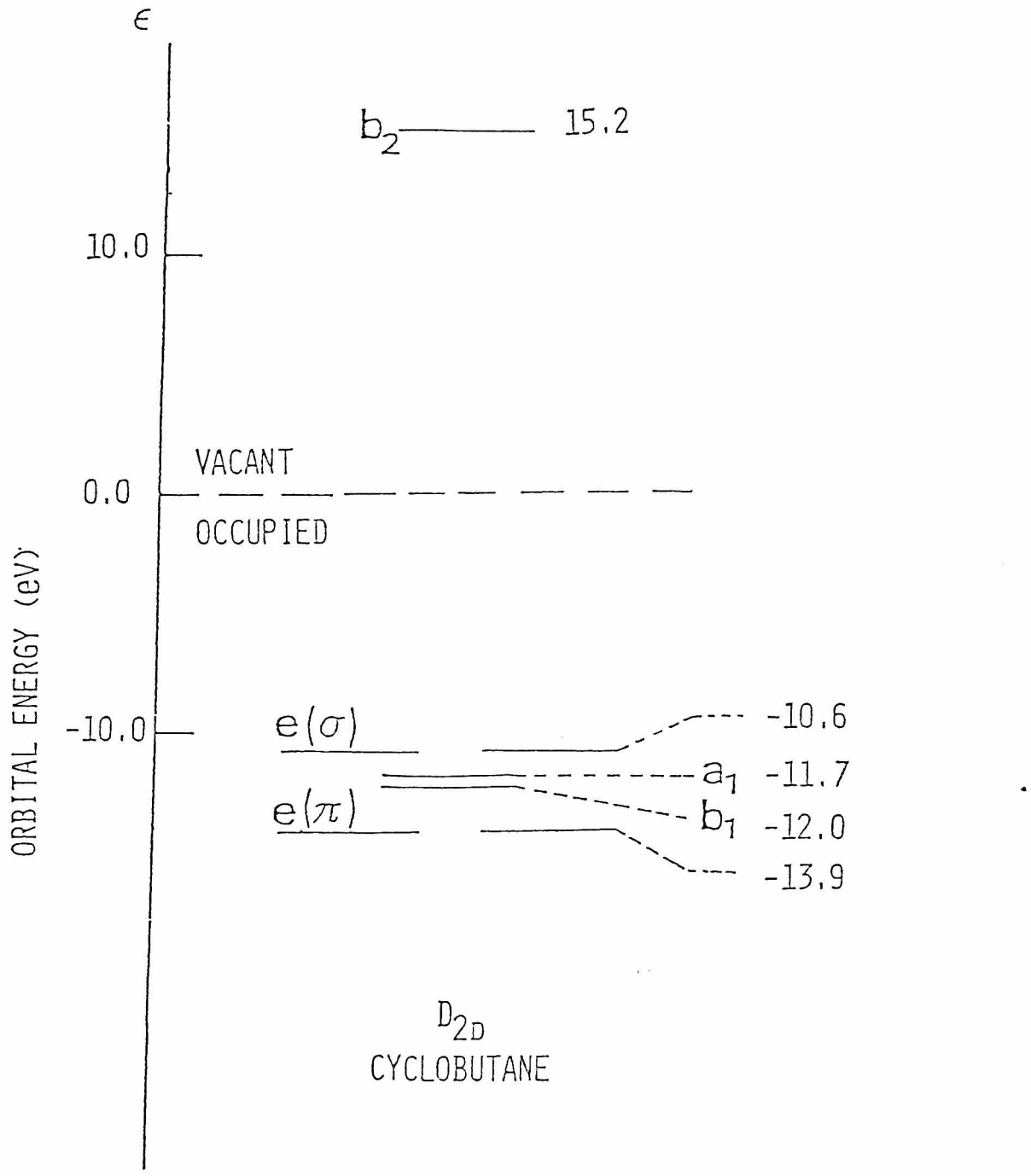

Figure 6. Orbital energy levels of neutral molecule of cyclobutane.

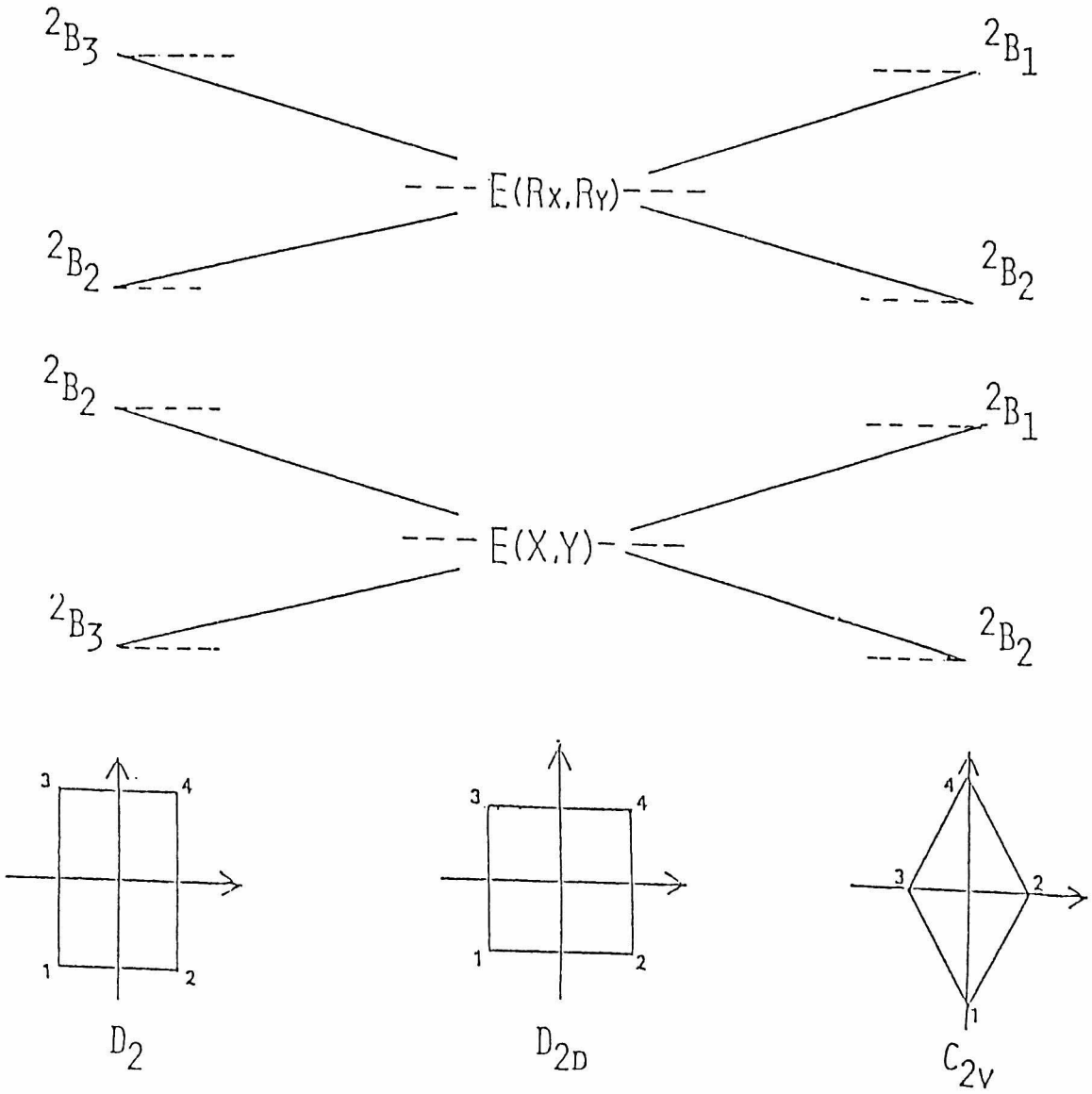

Figure 7. Correlation diagram of cation radical of cyclobutane. The $^2B_3$ state of D_2 symmetry is calculated to be 1.1 kcal/mol more stable than the $^2B_2$ state of C_{2v} symmetry.

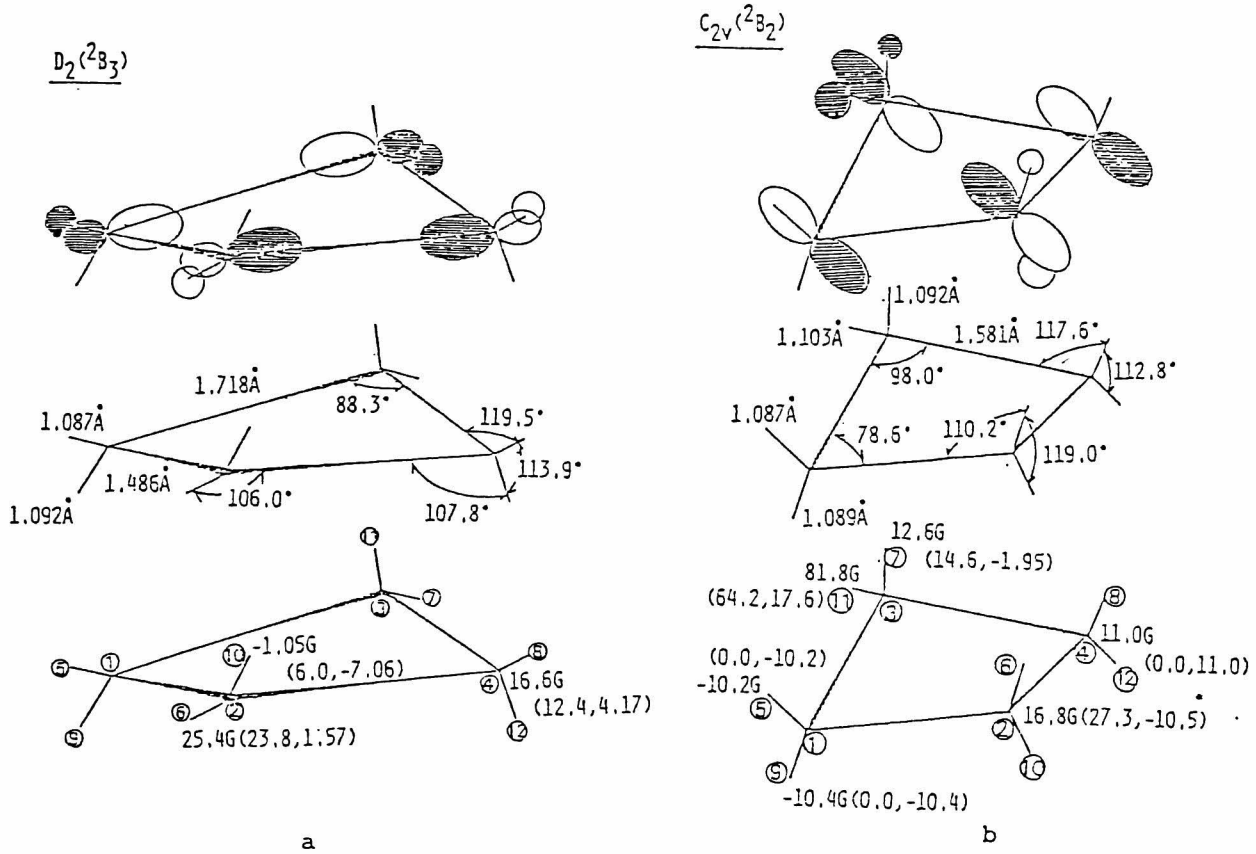

Figure 8. Nodal pattern of singly occupied orbital in the optimized geometry and hfs constants of cyclobutane cation radical. Experimental geometry of the neutral D_{2d} molecule is CC = 1.555Å, CH = 1.087Å, ∠CCC = 87.2°, ∠HCH = 108.6°. SD and SP contributions of hfs constants are given in the parentheses as (SD, SP) in gauss unit.

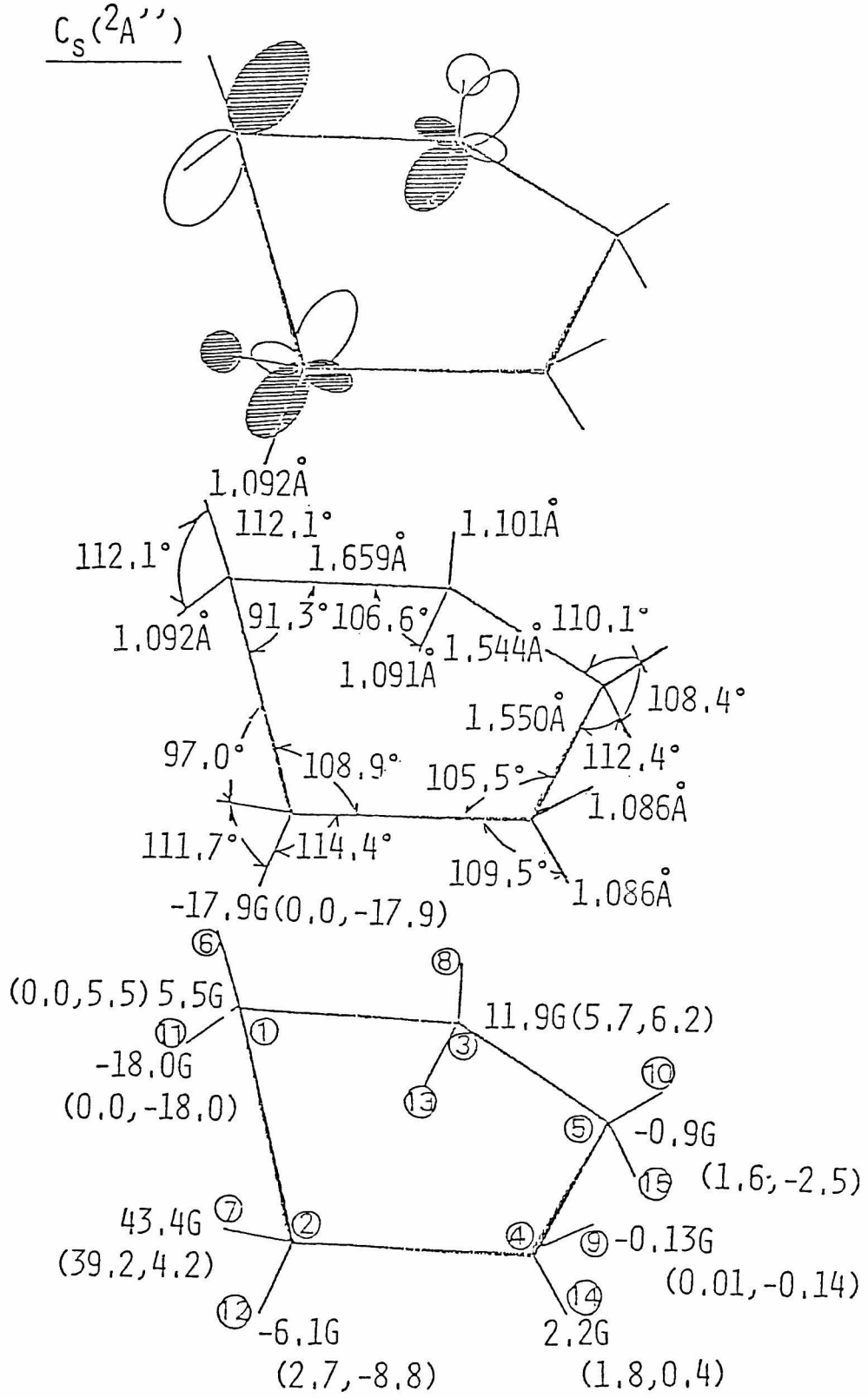

Figure 9. Nodal pattern of singly occupied orbital in the optimized geometry and hfs constants of cyclopentane cation radical. Experimental geometry of the nuetral D_{5h} molecule is CC = 1.52Å, CH = 1.09Å, ∠HCH = 109.5°. SD and SP contributions are given in the parentheses as (SD, SP) in gauss unit.

CHAPTER 4

SUMMARY

Here we applied the PO theory to the study of the spin correlation and molecular geometries in doublet radicals of chemical interests. In chapter 2, the spin density and molecular pyramidality of CH_3, SiH_3, and GeH_3 have been investigated. GeH_3 radical is calculated to be the most pyramidal and SiH_3 is the next. This rsult is parallel to the qualitative estimation based on the ESF theory though SiH_3 is reported to be most pyramidal based on the simple s-character estimation from the spin density obtained experimentally. The vibrational effect for the calculated hfs constants was found to be large especially for the central nucleus in these AH_3 radicals. The inner-shell spin polarizations changed largely for CH_3 and SiH_3 as the pyramidality angle varied and they were not always small. On the other hand, for GeH_3 radical, the inner-shell spin-polarizations were negligible and did not changed so largely when the molecular pyramidality changed. In chapter 3, we investigated the J-T distortion of cation radicals of cycloalkanes in ground and lower excited states. Calculated J-T distortions in the carbon frames or CH bonds were very large. The deformation of molecular geometry was parallel to the simple estimation from the nodal pattern of singly occupied orbitals. Hfs constants obtained by the PO theory reflected the large J-T distortion of the molecular geometry sensitively. If the dynamic J-T is assumed, calculated hfs constants agree well with the experimental results of cyclopropane and cyclopentane cation radicals.

GENERAL CONCLUSION

The spin and electron correlation problem is one of the most basic and interesting problems since the quantum mechanics has been applied to many electron systems. Theory of electron correlation and spin correlation is now an important branch of quantum chemistry. The nature of the correlation effect, which is absent in the Hartree Fock (HF) theory, is known to be short range in character and linked and unlinked terms of two-body excitation operators play an important role in the description of the electron correlation effect. The symmetry-adapted-cluster expansion (SAC) theory, due to Nakatsuji and Hirao, is a generalized cluster expansion theory to open-shell systems and excited states. The SAC-CI theory is based on the generalized Brillouin theorem of the SAC wavefunction. It gives a very natural and useful descriptions of various kinds of excited states.

In this thesis the author aimed to investigate the spin and electron correlations in open-shell systems and various excited states by using the SAC and SAC-CI theories and to examine the validity and applicability of these newly developed theories through the quantitative calculation.

In Part I of this thesis, the spin correlation problem has been studied by the pseudo-orbital (PO) theory. It includes only one-electron excitations within the SAC theory and is essentially within the orbital theoretic framework as the Thouless' theorem implies. The spin correlation effect of the PO theory has been shown to be superior to those of the conventional open-shell orbital theories, such as unrestricted

HF (UHF), spin extended HF (SEHF) theories. The self consistency of the spin correlation in the PO theory has also been studied with the use of iterative natural orbital technique. However, an iterative procedure including second-order terms seems to be superior to this technique.

In Part II, we studied the spin correlation, electron correlation, and the coupling thereof in various doublet radicals. Ground and excited states of various doublet radicals have been studied by the SAC and SAC-CI theories. These theories have given satisfactory result for valence and Rydberg excitation energies, ionization potentials, and spin densities of various doublet radicals. The coupling of spin and electron correlations has been shown to be large and various important spin distributions have been improved by the SAC and SAC-CI theories. Further the calculated results are independent of the choice of the molecular orbital in the reference configurations and the SAC and SAC-CI theories have been shown to include orbital reorganization effects enough in the open-shell and the lower excited states.

Part III gives the study of the valence and Rydberg excited states, ionized states, and electron attached states of formaldehyde. Calculated results have been satisfactory in comparison with the experimental values. The mixing of valence and Rydberg excitations in the $^1A_1$ ($\pi - \pi^*$) excited state has been studied. From the energetical point of view, this state is found to be valence in character. However, calculated second moment in this state, which gives a measure of the size of the electron cloud, has shown a small mixing of the Rydberg

character. For the Rydberg excited states, ionized states of NH_2 and CH_3 radicals, the SAC and SAC-CI theories have also given reasonable results in comparison with the experiments and the previous theoretical works.

The validity and applicability of the PO theory and the SAC and SAC-CI theories have been confirmed through the quantitative calculations shown in this thesis. In Part IV, the PO theory has been applied to the systems of chemical interests. First, the molecular geometry and spin correlations of doublet radicals which include heavier elements, such as Si and Ge, have been studied. The spin-polarization in inner-shells was found to be not always small and it changes largely as the molecular geometry varies. Vibrational effect for the molecular structures and the spin densities are also discussed. Lastly the spin densities and molecular geometries have been studied in the Jahn-Teller distorted geometries for cation radicals of cycloalkanes. In these σ radicals, the distribution of spin density has been coupled strongly with the molecular geometry and large spin densities have been evaluated as a reflection of large Jahn-Teller distortions in the ground and lower excited states.